Research on Arsenic Leaching from Coal Fly Ash under Different Environmental Conditions

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Abstract

In order to study the leaching behavior of arsenic from fly ash under different field conditions, this research used LEAF method 1313, 1314 and 1315 to test for the solid-liquid partitioning of arsenic under a range of solution pH and as a function solid-to-liquid ratio. The mass transfer rate of arsenic under diffusion-controlled release conditions was also tested. Results of these tests indicate that arsenic leaching from fly ash is highly pH-dependent. At different pH range, leaching concentration depends on the solubility of different dominant As species. In addition, the existence of other elements in fly ash also influence arsenic leaching despite of initial ash pH. The maximum flux usually occurs at the first leaching interval. Over time, arsenic leachate remains stable at a low lever after the leaching of most arsenic from the contacting surface. The simple radial diffusion model interpreted in the test method applies to all three fly ash tested follow. The effects of initial fly ash pH was also studied. Results show arsenic release decreases as solution pH increases from fly ash with alkaline pH. In addition, results indicate higher arsenic leaching concentrations from acidic fly ash than those from alkaline fly ash. These results agree with previous findings.

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Chapter 1

Introduction

In the United States, about 52 percent of the electricity produced comes from combustion of coal (USGS). In 2010, approximately 1048.3 million short tons of coal were consumed according to preliminary data from the U.S. Energy Information Administration (EIA) (Watson et al., 2010). The amount of coal consumption will continue increasing. This results in large amount of coal combustion products. Among coal combustion products, 60 percent of which consists of fly ash [Wiki]. Although about 43 percent of fly ash is recycled and reused, the rest usually goes into landfills.

Arsenic (As) is one of the toxic constituents of fly ash. It is hazardous to human health and the environment: causing lung, bladder, and skin cancer in people consuming arsenic-contaminated water over long periods of time (Dermatas & Moon, 2006). Arsenic contamination of ground water is found in many countries throughout the world, including the United States. Arsenic exists in four oxidation states, arsenate (+V), arsenite (+III), arsenic (0), and arsine (−III) (Sharma & Sohn, 2009). A wide range of arsenic toxicity has been determined that depends on arsenic speciation. Generally inorganic arsenic species are more toxic than organic forms to living organisms, including humans and other animals (Goessler and Kuehnett, 2002; Meharg and Hartley-Whitaker, 2002; Ng, 2005). Leachate samples from fly ash landfills have shown a range of arsenic concentrations from 1.4 up to 1380 µg/L with a median of 25 µg/L (Tennessee Valley Authority, 2010). The arsenic standard set by US Environmental Protection Agency (USEPA) for drinking water is at 10 ppb (9.99 µg/L). Therefore, it is important to understand the

leachate behavior of arsenic from fly ash landfills to aquatic systems in order to help find the optimum landfill conditions.

Due to its known toxic and carcinogenic properties, there has been significant research investigating mechanisms and processes responsible for arsenic release to aquatic systems. From fly ash, leaching of arsenic depends on a number of factors including pH, oxidation levels, solid-to-liquid ratio, and types of coal (Tennessee Valley Authority, 2010). A number of researchers have investigated the influence of different parameters on the leachability of inorganic constituents from fly ash, including arsenic. For example, the leachability of arsenic from fly ash increases with lower leachate pH values and high temperatures (Baba & Gurdal & Sengunalp & Ozay, 2007). However, most research focused only on the influence of one parameter. In order to study the leachate behavior of arsenic from fly ash under different field conditions, this research will evaluate three different parameters including (1) solution pH, (2) liquid-to-solid ratio on liquid-solid partitioning, and (3) mass transfer rate under controlled mass conditions.

1.1 Method Background

This research used the leaching test methods (Method 1313, 1314 and 1315) developed by the Leaching Environmental Assessment Framework. The framework recommends a collection of four leaching tests that can be used to develop a characteristic leaching profile of the subject material under the influence of physical and chemical factors.

During the process of leaching, constituents from a solid material are released into a contacting liquid. It includes the partitioning of contaminants between a solid and liquid phase along with the mass transport of aqueous or dissolved constituents. The leaching process is affected by certain factors that can alter the rate or extent of leaching. As shown in Figure 1, important

chemical factors, those that influence the liquid-solid partitioning (LSP) of a constituent, include solution pH, redox, the presence of dissolved organic matter, and biological activity. Physical factors, such as relative hydraulic conductivity, porosity and fill geometry, play an important role in determining the rate at which constituents transport through a solid into a passing liquid phase.

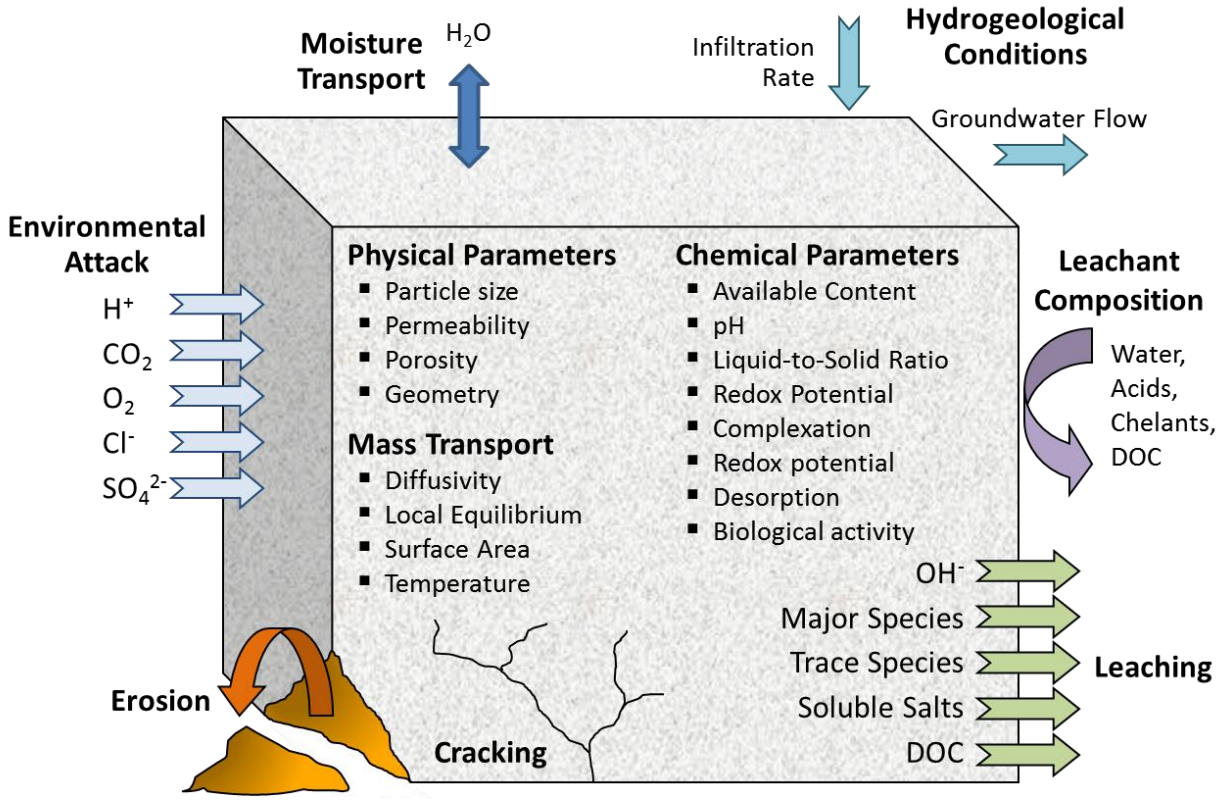

Figure 1. Physical and Chemical Factors Influencing Leaching

Therefore, each of these four tests is designed to study one release-controlling parameter (e.g., pH, liquid-to-solid ratio) to provide leaching behavior of test target over a broad range of test conditions. This research will use test method 1313, 1314 and 1315 to evaluate the liquid-solid partitioning under the influence of solution pH and liquid-to-solid ratio as well as the mass transfer rate of arsenic from three fly ash samples.

1.2 Fly Ash Samples

Fly ash samples from eight power plants were collected for preparation for this research. These fly ash samples were named using the names of the power plants where they were generated: Clifty Creek fly ash, Rockport fly ash, Kanawha River fly ash, Amos fly ash, Mountaineer fly ash, Gavin fly ash, Sammis fly ash, and Fort Martin fly ash. These samples were selected because they gave a range of solution pH after added to certain amount of deionized water. Three of these samples were selected after a pre-test for the initial solution pH of the fly ash: Rockport fly ash, Kanawha River fly ash, and Fort Martin fly ash. Leaching tests were then performed for each sample to evaluate the influence of solution pH and liquid-to-solid ratio on the partitioning of arsenic as well as the mass transfer rate. Further comparisons between these samples were made to study the influence of their initial solution pH values on arsenic leaching behavior. Two of the selected fly ashes were sent out for element composition analysis. The rest one sample was collected later, therefore was not sent out for the element composition analysis. The original arsenic concentrations were 32.657 μg As/ g ash and 36.324 μg As/ g ash in Rockport and Kanawha River fly ash respectively. A table containing concentrations of all tested elements in fly ash is provided in Appendix.

1.3 Objectives

As stated above, there are four objectives for this research: (1) study the solid-liquid partitioning of arsenic under a range of solution pH; (2) study the solid-liquid partitioning of arsenic as a function of solid-to-liquid ratio; (3) determine the mass transfer rate of arsenic under diffusion-controlled release conditions; and (4) compare arsenic leaching results between three fly ash samples with acidic, neutral, and alkaline initial solution pH. Insight understanding of arsenic

leaching behavior under different environmental conditions will help develop effective ways of reducing its release to the environment, therefore minimizing its influence on human health.

Chapter 2

Materials and Methods

The research used three fly ash samples selected based on their initial solution pH. A pre-test for fly ash pH was conducted according to section 6.8 of *Standard Practice for Characterizing Fly Ash for Use in Soil Stabilization* (Designation D5239-12). Approximately 20 grams of each fly ash sample and 80 mL deionized water were added in to a covered beaker. The mixtures were stirred to disperse the fly ash and then left undisturbed for 2 hours. After that, solution pH of each sample was determined using a pH meter. Rockport fly ash, Kanawha river fly ash and Fort Martin fly ash were selected for having basic, neutral and acidic pH values.

Sample	Mass added (g)	DI water added (mL)	pH
Clifty Creek fly ash	20	80	11.2
Rockport fly ash	20	80	11.3
Amos fly ash	20	80	9.1
Kanawha River fly ash	20	80	7.8
Gavin fly ash	20	80	9.48
Mountaineer fly ash	20	80	8.7
Sammis fly ash	20	80	10.65
Fort Martin fly ash	20	80	3.83

Table 1. Initial pH Values of Selected Fly Ash Samples

2.1 Method 1313

LEAF Method 1313 is called *Liquid-Solid Partitioning (LSP) as a Function of Eluate pH for Constituents in Solid Materials Using a Parallel Batch Extraction Procedure*. It is used to generate a liquid-solid partitioning curve of arsenic as a function of solution pH. Aqueous extracts at seven target pH values from pH 2 through 10.5 were obtained. Eluate concentrations for arsenic will be determined and plotted as a function of solution pH.

The main part of this method is parallel batch extractions of solid material with addition of either dilute acid or base. Particle size reduction of samples may be required to make sample particles homogeneous and to minimize mass transport through large particles. According to table 2, minimum dry mass of sample, contact time and vessel size needed for parallel batch extractions can be determined. For all three fly ash, 85 weight-percent sample particle is smaller than 0.3mm. Therefore, the extraction experiment requires 20 ± 0.02 grams dry sample, 24 ± 2 hours contact time and 250 mL vessels.

Particle Size (85 wt% less than) (mm)	US Sieve Size	Minimum Dry Mass (g-dry)	Contact Time (h)	Suggested Vessel Size (mL)
0.3	50	20 ± 0.02	24 ± 2	250
2.0	10	40 ± 0.02	48 ± 2	500
5.0	4	80 ± 0.02	72 ± 2	1000

Table 2. Extraction Parameters as Function of Maximum Particle Size using LEAF Method 1313

The moisture content of each fly ash sample was determined in order to calculate the required mass that contain 20 ± 0.02 grams dry sample. Moisture content for both Rockport fly ash and Kanawha River fly ash was 0.056%, therefore were considered dry. For Fort Martin, the moisture content was determined to be 0.317%, also considered as dry.

In order to determine the amount of acid or base required for certain pH, a pre-test titration is required. For both pre-test titration and parallel batch extractions, 2L of 2N nitric acid (HNO_3) and 1L of 1N sodium hydroxide (NaOH) were used. To prepare 2L of 2N HNO_3, 359.50 grams of 15.8N HNO_3 (stocked in the lab) and enough DI water were added into a 2L volumetric flask. The solution were thoroughly mixed. For 1L of 1N NaOH, 56.16 grams of solid NaOH and enough DI water were added to a 1L volumetric flask and thoroughly mixed. To determine the

pre-test acid-base schedule, the classification of the neutralization behavior of each fly ash was predicted. Fly ash is considered with low alkalinity. A pre-test acid-base schedule was generated based on initial pH and other prior knowledge for each fly ash. For each fly ash, 6 pre-titration samples were made by adding 10 grams fly ash, certain amount of DI water and acid or base to a 200 mL vessel. The liquid-to-solid ratio has to be 10 mL/g. After tumbling all vessels in an end-over-end fashion at a speed of 28 ± 2 rpm at room temperature for 24 hours, pH values of each solution was measured. A pre-test titration curve, the extract pH as a function of the equivalents of acid or base added, was generated. Tables (Table 3, 4 and 5) with information regarding the amount of acid or base and DI water as well as the resulting pH for each pre-titration sample are provided below for all three fly ash.

Kanawha River	Initial pH 7.8					
Vessel	K1	K2	K3	K4	K5	K6
Fly ash sample added (g)	10	10	10	10	10	10
Acid added (mL)	0.125	0.25	2			
Base added (mL)				0.5	0.25	0.1
DI water added (mL)	99.875	99.75	98	99.5	99.75	99.9
pH	6.71	4.37	2.09	10.56	9.75	9.13

Table 3. Pre-titration Acid-Base Schedule for Kanawha River Fly Ash

Rockport	Initial pH 11.3					
Vessel	R1	R2	R3	R4	R5	R6
Fly ash sample added (g)	10	10	10	10	10	10
Acid added (mL)	5	15	30	45	75	2.5
Base added (mL)						
DI water added (mL)	95	85	70	55	25	97.5
pH	8.14	6.91	5.14	3.46	2.7	9.14

Table 4. Pre-titration Acid-Base Schedule for Rockport Fly Ash

Fort Martin	Initial pH 3.84					
Vessel	F1	F2	F3	F4	F5	F6
Fly ash sample added (g)	10	10	10	10	10	10
Acid added (μL)						
Base added (μL)	1000	500	100	60	20	10
DI water added (mL)	99	99.5	99.9	99.94	99.98	99.99
pH	10.82	9.75	9.2	8.38	8.48	8.34

Table 5. Pre-titration Acid-Base Schedule for Fort Martin Fly Ash

After that, an acid-base schedule for parallel batch extractions of each fly ash sample was created based on the pre-titration curve generated using data from Table 3, 4 and 5. The steps for parallel batch extraction were the same as those for pre-titration test except for 20 grams of sample was used instead of 10 grams. Therefore, 20 grams fly ash, predicted amount of acid or base with enough DI water were added into a 250 mL vessel, giving a liquid-to-solid ratio of 10 mL extract/g-dry fly ash. Seven parallel batch extractions with pH range of 2.0 to 10.5 were designed for each fly ash. The vessels then were tumbled in an end-over-end fashion at a speed of 28 ± 2 rpm at room temperature for 24 hours. Eluate from each extraction was collected and preserved with 2 mL 1N HNO_3/ 100mL eluate. pH values, conductivity as well as arsenic concentration was measured after vacuum filtration with glass fiber filter paper (0.70 μm pore size). Arsenic concentration in the eluate was measured using an 880Z Atomic Absorption Spectrometer.

The acid-base schedule of each fly ash was provided in the following tables (Table 6, 7 and 8). For Fort Martin fly ash, 4 instead of 9 extractions were designed due to its relatively low buffer ability. More explanation is provided in the result chapter.

Kanawha River	Initial pH 7.8						
Vessel	K1	K2	K3	K4	K5	K6	K7
Target pH	10.5	9.0	8.0	7.0	5.5	4.0	2.0
Fly ash sample added (g)	20.1	19.8	20.2	20.1	20.1	20.1	20.0
Acid added (µL)				180	370	750	3000
Base added (µL)	1000	200	25				
DI water added (mL)	199.2	199.7	199.9	199.8	199.7	199.4	197.2

Table 6. Acid-Base Schedule for Parallel Batch Extractions of Kanawha River Fly Ash

Rockport	Initial pH 11.3						
Vessel	R1	R2	R3	R4	R5	R6	R7
Target pH	10.5	9.0	8.0	7.0	5.5	4.0	2.0
Fly ash sample added (g)	20.1	20.0	20.1	20.1	20.1	20.0	20.1
Acid added (mL)	2	6.65	12	28	53	80	170
Base added (mL)							
DI water added (mL)	198.3	193.5	188.0	172.0	147.0	120.0	30.0

Table 7. Acid-Base Schedule for Parallel Batch Extractions of Rockport Fly Ash

Fort Martin	Initial pH 3.84			
Vessel	R1	R2	R3	R4
Target pH	10.5	9.0	8.0	4.0
Fly ash sample added (g)	20.1	20.0	20.1	19.8
Acid added (µL)				
Base added (µL)	2200	200	25	0
DI water added (mL)	197.8	199.8	199.98	200.0

Table 8. Acid-Base Schedule for Parallel Batch Extractions of Fort Martin Fly Ash

2.2 Method 1314

LEAF Method 1314 is called *Liquid-Solid Partitioning as a Function of Liquid-to-Solid Ratio for Constituents in Solid Materials Using a Percolation Column Procedure*. This method was used for studying liquid-solid partitioning of arsenic in the fly ash as a function of liquid-to-solid ratio. When using this method, fly ash sample is moderately packed into a column with leaching

solution (DI water) introduced in an up-flow pumping mode. Up-flow pumping is used here to avoid air entrainment and flow channeling. The introducing flow rate should be maintained between 0.5 and 1.0 L/S per day. In other words, the volume of injected leaching solution in mL should be between half of or equal to the mass of packed solids in gram. Eluate is collected based the schedule of leaching intervals, as a function cumulative L/S.

As stated before, 85 weight-percent of each sample particle is smaller than 0.3mm. Therefore, particles of all three fly ash were smaller than the maximum acceptable particle size. In addition, moisture contents for Rockport, Kanawha River and Fort Martin fly ash were 0.056%, 0.056% and 0.317% respectively.

2.2.1 Column Preparation

Three straight cylindrical columns, each of 30-cm height and 5-cm inner diameter, were used. All columns were constructed of inert material, resistant to high and low pH conditions and interaction with arsenic. Volumes of each column were sufficient to accommodate a minimum a 300-g dry material as well as two 1-cm layers of silica sand. The silica sand was used at the bottom of the column to distribute leaching solution and at the top to form a coarse filter for eluate particulates. The column was sealed with leak-proof end caps at both sides.

One end cap was secured to the column at first. The masses of each empty column with end cap on one side were recorded. About 1-cm thick layer of quartz sand was added to the column. Each column with one sand layer was weighed with sealed side facing downward. Each fly ash material was added to the column in five layers with light tamping to level the material between each layer. In each column, enough test material was added, leaving the top of the packed sample about 1 cm from the level of the column interface with the other end cap. The column with one

sand layer, one end cap and dry fly ash was weighed. Another layer of sand was placed between top of sample material and the interface between the column and the other end cap. The other side of each column was sealed with the other end cap. The masses of each sample were calculated and converted to the dry mass equivalents.

After preparation of each column, two tubes were connected to both sides, one for introducing leaching solution and the other for eluate collection. A pump was used to provide a flow rate that could lead to an eluate production rate between 0.5 and 1.0 L/S per day. The other end inlet tube was connected to a tank containing about 5 L DI water. The inlet tube was rinsed with DI water before it was connected to inflow end of the column. The outlet tube was connected to a stock container for collecting eluate. The container used was made of inert material and was large enough to store the outflow during the longest leaching interval. Table 9 below provides dry masses of each sample material added and the average L/S ratios. The average L/S ratio for Rockport fly ash was excess the range of 0.5-1.0 as specified by this method. The lowest flow rate generated by the available pump was used and still led to a L/S ratio excess the range.

Sample	Sample added (g)	Dry mass equivalent (g)	Average L/S ratio
Fort Martin	699.2	697.0	0.84
Kanawha River	516.7	516.4	0.81
Rockport	620.6	617.1	1.10

Table 9. Dry Masses of Samples and Average Liquid-Solid Ratios

2.2.2 Column Test

Each column was placed on a holder with inlet tube facing downward. The pump was turned on to allow the column to fill with leaching solution. After the column was completely wetted with leaching solution filled the whole column, the pump was turned off. The column was then left undisturbed for equilibration for about 16 hours.

After equilibration, the pump was turned on and the time and date was recorded. Eluate was collected and tested for each interval according to the schedule generated using the template provided by LEAF for this method. The start point of the next interval was generated based on the flow rate during the previous interval. The actual starting time and date was recorded for each interval for the generation of next start point. The flow rate for each column test was monitored frequently to maintain the L/S ratios in Table 9. After each interval, eluate was tested for pH and conductivity. Approximately 50 mL of each eluate was collected from the stock container and preserved with 2% eluate volume of 2N HNO3. The preserved sample was measured for arsenic concentration using an 880Z Atomic Absorption Spectrometer. Tables of scheduled intervals for each sample are provided in the appendix.

2.3 Method 1315

LEAF Method 1315 is called *Mass Transport Rates of Constituents in Monolithic or Compacted Granular Materials Using a Semi-dynamic Tank Leaching Procedure*. This test is used for testing mass transfer rates of arsenic from fly ash under mass transfer controlled conditions. A granular material such as fly ash will be compacted into a cylindrical mode and go through tank leaching in DI water. The leaching solution will be renewed periodically according to a pre-determined schedule. The fly ash will be compacted using modified Proctor compaction at its optimum moisture content. Fly ash sample will be in contact with fresh DI water at nine intervals. Eluate of each interval will be collected and measured for arsenic concentration and conductivity.

2.3.1 Optimum Moisture Content Test

In order to provide a uniform approach to obtain a sample density that approximates field conditions, the fly ash sample should be compacted at a moisture content corresponding to 90% of the modified Proctor optimum packing density. Optimum moisture content is the fractional mass of water in the sample that presents at the optimum packing density. The method for determining optimum moisture content of fly ash is described in reference document ASTM D698-07. The original moisture content of each fly ash was determined. All three sample were considered dry.

Moisture Content:							
Test Number	1	2	3	4	5	6	7
Name of can	#16	#14	F-3	1/11	#12	1/17	1/13
Mass wet soil (g)	152.68	149.71	150.19	150.44	150.17	149.6	150.22
Mass dry soil (g)	133.16	127.3	126.05	124.74	119.58	116.14	117.03
Mass water (g)	19.52	22.41	24.14	25.7	30.59	33.46	33.19
Water Content (%)	14.7%	17.6%	19.2%	20.6%	25.6%	28.8%	28.4%

Table 10. Actual Water Contents Determined

Density and Unit Weight:							
Test Number	1	2	3	4	5	6	7
Estimated Water Content (%)	15.0%	18.0%	20.0%	22.0%	25.0%	29.0%	27.0%
Water Content (%)	14.7%	17.6%	19.2%	20.6%	25.6%	28.8%	28.4%
Mass of soil (g)	1461.5	1530.8	1561.3	1600.5	1694.5	1669.3	1617.8
Volume of mold (ft^3)	0.03312	0.03312	0.03312	0.03312	0.03312	0.03312	0.03312
Wet unit weight (lbf/ft^3)	97.28	101.90	103.93	106.54	112.79	111.12	107.69
Dry unit weight (lbf/ft^3)	84.85	86.64	87.22	88.34	89.82	86.26	83.90

Table 11. Wet and Dry Unit Weight Determined

Seven samples of Fort Martin fly ash were made by mixing 2.3kg fly ash and enough DI water to give water contents bracket the estimated optimum water content. Selected moisture contents varied by 2%. After standing for 16 hours, each sample was compacted into a mold that was secured to a base plate using a 10-lb cylindrical concrete. The sample was compacted in three layers, with 25 blows on each layer. The mass of sample in mold was determined and recorded. A wet unit weight was calculated using the sample mass and mold volume for each sample. A portion (about 200 grams) of each prepared sample was weighed, dried at 105 °C for 48 hours, and reweighed for calculating its actual moisture content. Then a dry unit weight was determined. A plot of dry unit weight of all seven samples versus their water contents was generated. The maximum dry unit weight of that type of fly ash was determined. The data for optimum moisture content determination is provided in Table 10 and 11 above. The plot of dry unit weight versus water contents is also provided below (Figure 2). The optimum moisture content for Fart Martin fly ash was determined as 25%.

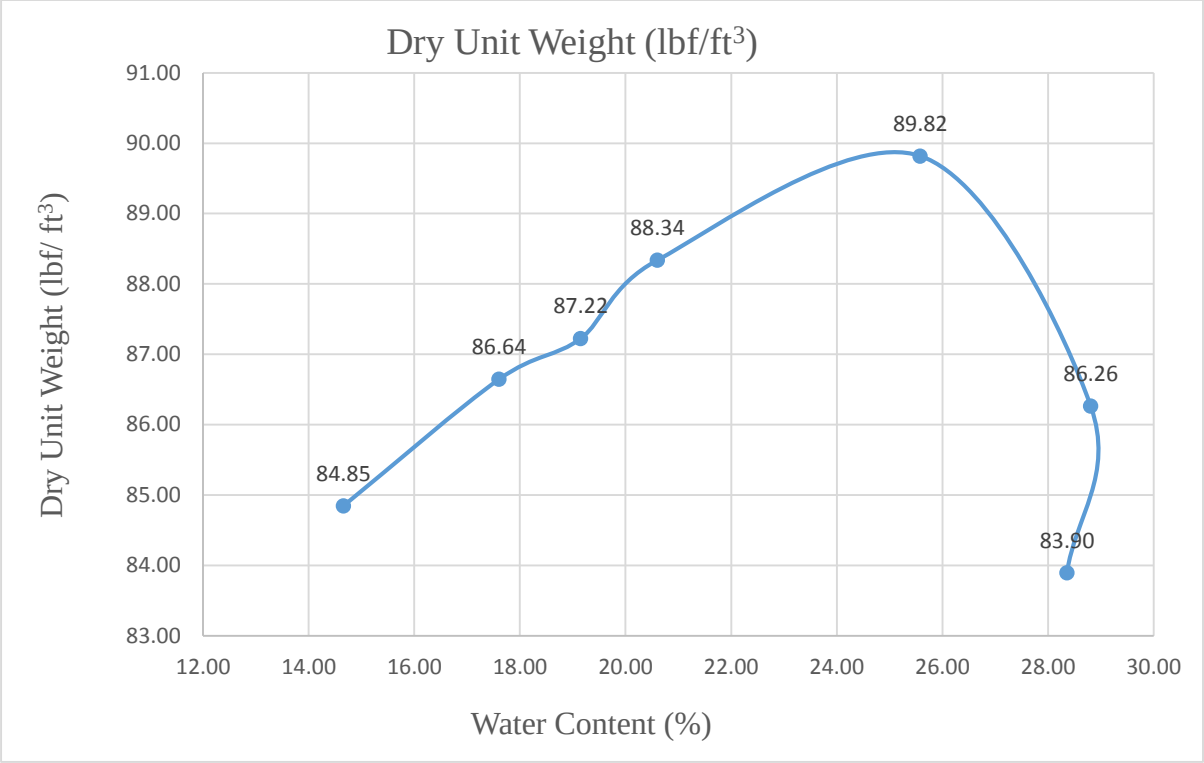

Figure 2. Dry Unit Weight versus Water Content

Optimum moisture contents for Kanawha River fly ash and Rockport fly ash were not determined following this test method because very long period of time and large amount of fly ash sample were required when using this method. Optimum moisture contents for those two samples were estimated based on prior acknowledge and several compaction attempts. The optimum moisture content for Kanawha River fly ash was estimated as 27% while that for Rockport fly ash was 21%.

2.3.1 Tank Leaching

For tank leaching, compacted fly ash sample in a vessel (an open faced cylinder) was placed in a cylindrical tank filled with leaching solution (DI water). The vessel and sample dimensions were chosen so that the sample was completely immersed in the leaching solution. The vessel for each tank leaching test met requirement of Method 1315 that the sample holder must be composed of

an impermeable material or other material resistant to high and low pH. The distance between wall of vessel and that of leaching tank was less than 0.5 cm as required by this method. A minimum sample size of 5 cm in the direction of mass transfer is required. The ratio of total liquid volume to the contacting area must be maintained at 9 ± 1 mL/cm^2.

For each fly ash, 1000 g of dry fly ash was used to make the leaching sample at its optimum moisture content. Table 12 below provides the total masses of each tank leaching sample made by mixing the shown masses of dry sample and volumes of DI water. Each sample was compacted into a vessel in 5 layers with 13 blows for each layer as suggested by the method. The final masses in the vessels are 724.7g, 589.7g and 752g for Fort Martin, Kanawha River and Rockport fly ash respectively.

Fly ash sample	Optimum MC (%)	Initial MC (%)	Dry sample added (g)	DI water added (mL)	Total sample mass (g)
Fort Martin	25	0.317	1000	246.8	1246.83
Kanawha River	27	0.056	1000	269.4	1269.44
Rockport	21	0.056	1000	209.4	1209.44

Table 12. Data Needed for Preparing Leaching Samples for Compaction

Vessels containing compacted fly ash was placed in cylindrical tanks each with diameter of 11.1 cm and height of 13.5 cm. The diameter of each vessel was 10.2 cm. For the volume of leaching solution added, equation $V = \pi \times \left(\frac{D}{2}\right)^2 \times (L/A)$ was used. $V = \pi \times \left(\frac{10.2\ cm}{2}\right)^2 \times (9\ mL/cm^2) = 735\ mL$. However, after compacting the fly ash to a height of 6 cm in the direction of mass transfer and placing it in tank, the volume left above the sample was less than 735 mL. Therefore, a volume of 700 mL was used. The subtraction of 35 mL of leaching solution still led to L/A ratio within 9 ± 1 mL/cm^2.

After preparation of tank leaching samples, they were covered with air-tight lid and kept undisturbed until the end of the leaching interval. The schedule of leaching intervals is provide in Table 13 (provided by Method 1315) below. At the end of each leaching interval, the vessel was removed from the tank and kept undisturbed before placed in the tank with refresh solution. The eluate was collected, tested for pH and conductivity and preserved with 2% eluate volume of 2N HNO_3. The tank was cleaned and filled with 700 mL DI water. The vessel was then placed in the tank with care and covered with airtight lid. The sample was kept undisturbed before the end of the interval. The preserved sample was measured for arsenic concentration using an 880Z Atomic Absorption Spectrometer.

Interval Label	Interval Duration (h)	Interval Duration (d)	Cumulative Leaching Time (d)
T01	2.0 ± 0.25	–	0.08
T02	23.0 ± 0.5	–	1.0
T03	23.0 ± 0.5	–	2.0
T04	–	5.0 ± 0.1	7.0
T05	–	7.0 ± 0.1	14.0
T06	–	14.0 ± 0.1	28.0
T07	–	14.0 ± 0.1	42.0
T08	–	7.0 ± 0.1	49.0
T09	–	14.0 ± 0.1	63.0

Table 13. Schedule of Each Leaching Interval and Cumulative Leaching Time

Chapter 3

Results and Discussion

3.1 pH Dependence Analysis

Figure 3, 4 and 5 below provide titration curves of eluate pH values as a function of acid (positive value in meq/g-dry) or base (negative value in meq/g-dry) added to each fly ash sample. For Kanawha River and Rockport fly ash, eluate pH values were very close to targeted pH values. For Fort Martin, many pre-titrations were conducted in order to achieve a range of 2.0 to 10.5 pH values. However, only pH values larger than 8.0 were obtained with the addition of base. Despite of its initial acidic pH, pH of the solution made with Fort Martin fly ash and pure DI water became above 8.0 after 24-hour mixing as specified by Method 1313. Therefore, a titration curve of only 4 pH values as a function of base added was generated. One possible reason for this is the ash tends to develop more neutral pH values as pH-controlling elements migrate with water percolation over time (Izquierdo & Querol, 2012). The amounts of elements on the ash surface that can react with the added base might be considerably small. Therefore, pH changes rapidly from acidic to around neutral. Addition of acid to Fort Martin sample may be tried in order to obtain pH value less than 8.0 for further research.

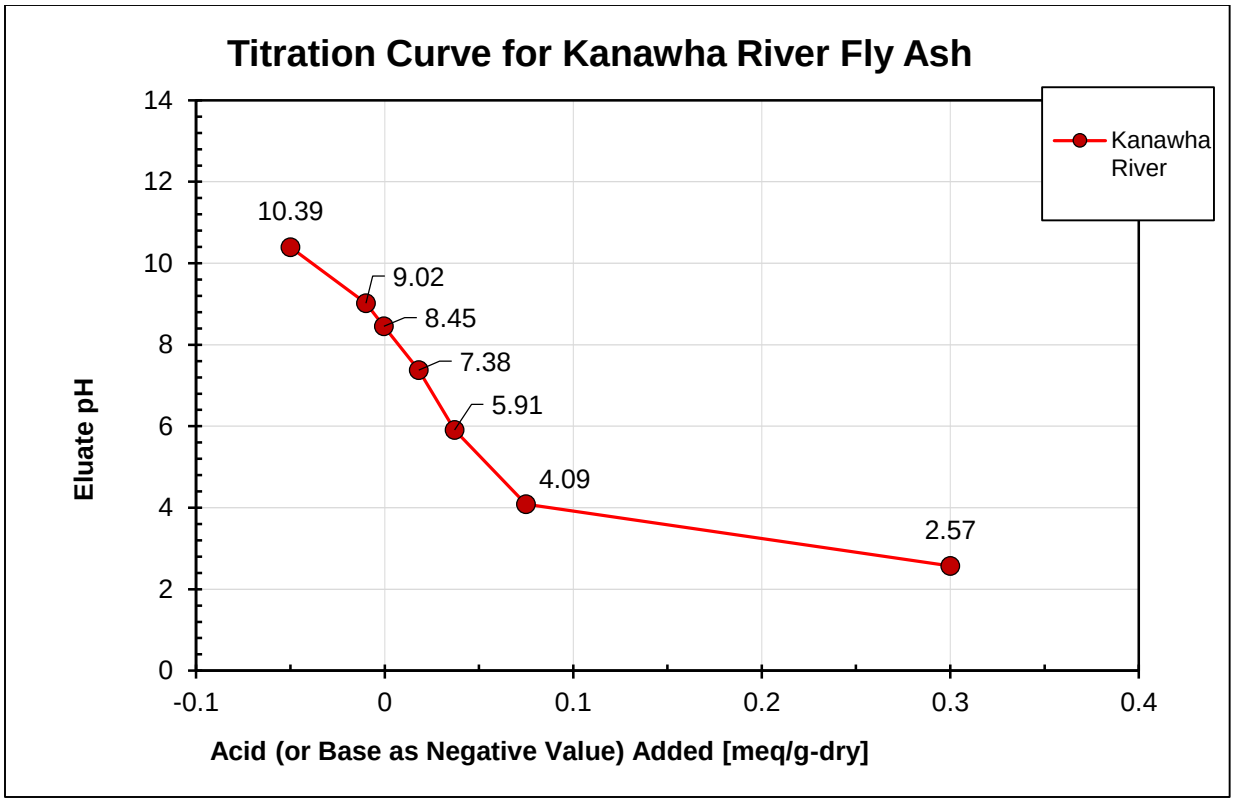

Figure 3. Titration Curve for Kanawha River Fly Ash

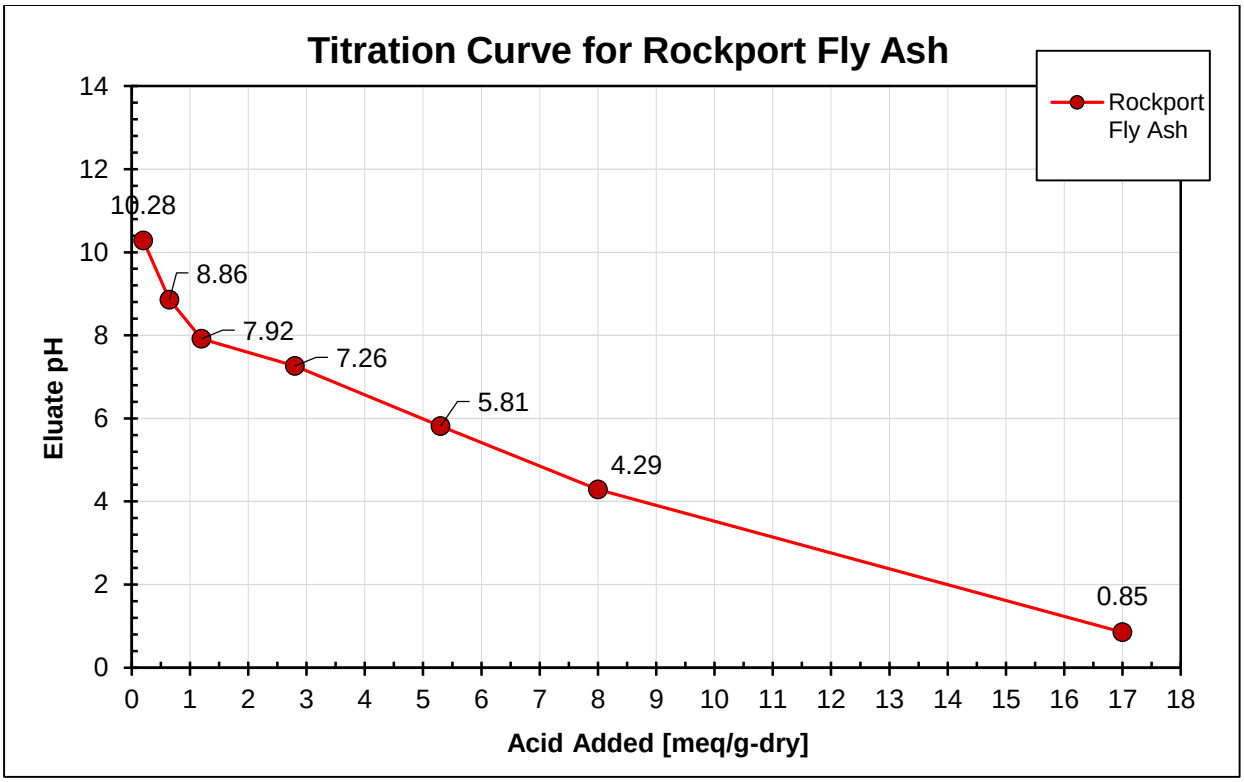

Figure 4. Titration Curve for Rockport Fly Ash

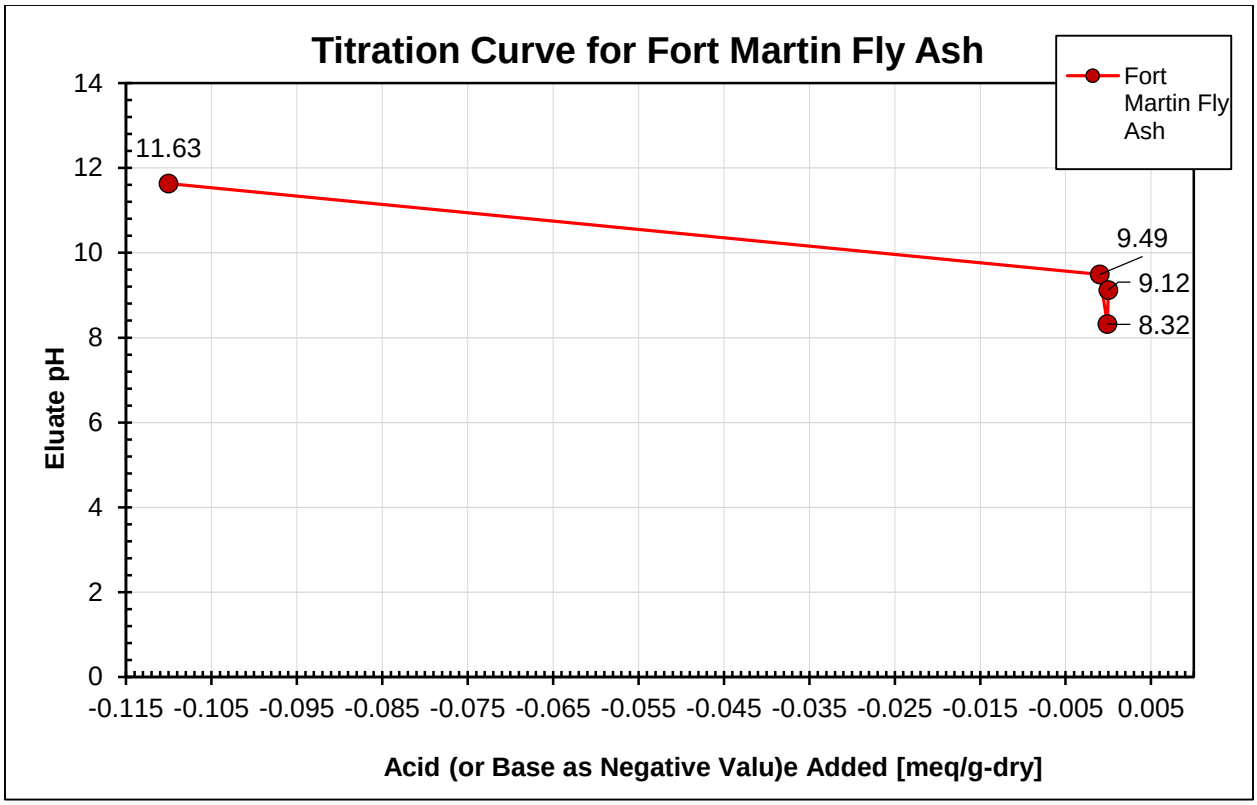

Figure 5. Titration Curve for Fort Martin Fly Ash

The liquid-solid partitioning curve was generated by plotting arsenic concentrations in the aqueous phase as a function of the measured solution pH as shown in Figure 6, 7 and 8. All plots were in different patterns. For Kanawha River fly ash, arsenic concentration decreased as eluate pH increased from 2.57 to around 6.0. As pH increases from 6.0 to 10.39, As concentration increased to a peak of 103.73 µg/L at around 9.0 and then started decreasing again. For Rockport fly ash, as pH value increased from 0.85 to 10.28, As concentration fluctuated with 2 peaks at pH 5.81 and pH 8.86 and 2 lows at pH 4.29 and pH 7.26. For Fort Martin fly ash, As concentration first increased as pH increases from 8.32 to 9.12 and then decreased as pH increased from 9.12 to 11.63.

Although the curve patterns of each fly ash were different, there were several similarities. For all three fly ash samples, arsenic concentration decreased starting from pH of 9. In addition, for Kanawha River and Rockport fly ash, arsenic concentration was highest at very low pH level (below 2). As the flue gas cools down after combustion, arsenic condenses on the surface of the fly ash particles, forming compounds with a variable solubility. The solubility of those compounds is affected by the solution pH (Izquierdo & Querol, 2012). Of the several forms of arsenic, As (III), As (V) undergo acid–base equilibria, thus different major and minor species will be present depending on the pH values (Sharma & Sohn, 2009). At neutral pH, As (III) is present as a neutral species, $As(OH)_3$ (IAEA, 2007). At alkaline pH range, $As(OH)_3$ dissociates to $As(OH)_2^{2-}$and insignificant amount of $As(O_3)^{3-}$. At lower pH, $AsO_2(OH)_2{}^-$(As V) is the dominant species. At pH 7, about half of $AsO_2(OH)_2{}^-$dissociates to $AsO_3(OH)_2{}^{2-}$. At alkaline pH, As (V) presents in the form of AsO_4^{3-}(Sharma & Sohn, 2009).

According to Method 1313, there are four characteristic liquid-solid partitioning (LSP) curve shapes. The shape of the resulting LSP curve of each fly ash is indicative of the speciation of arsenic in the solid phase. Comparing the resulting LSP curves to LSP curves in Figure 9, LSP curves for both Rockport fly ash and Kanawha River fly ash were similar to the characteristic curve for oxyanionic species.

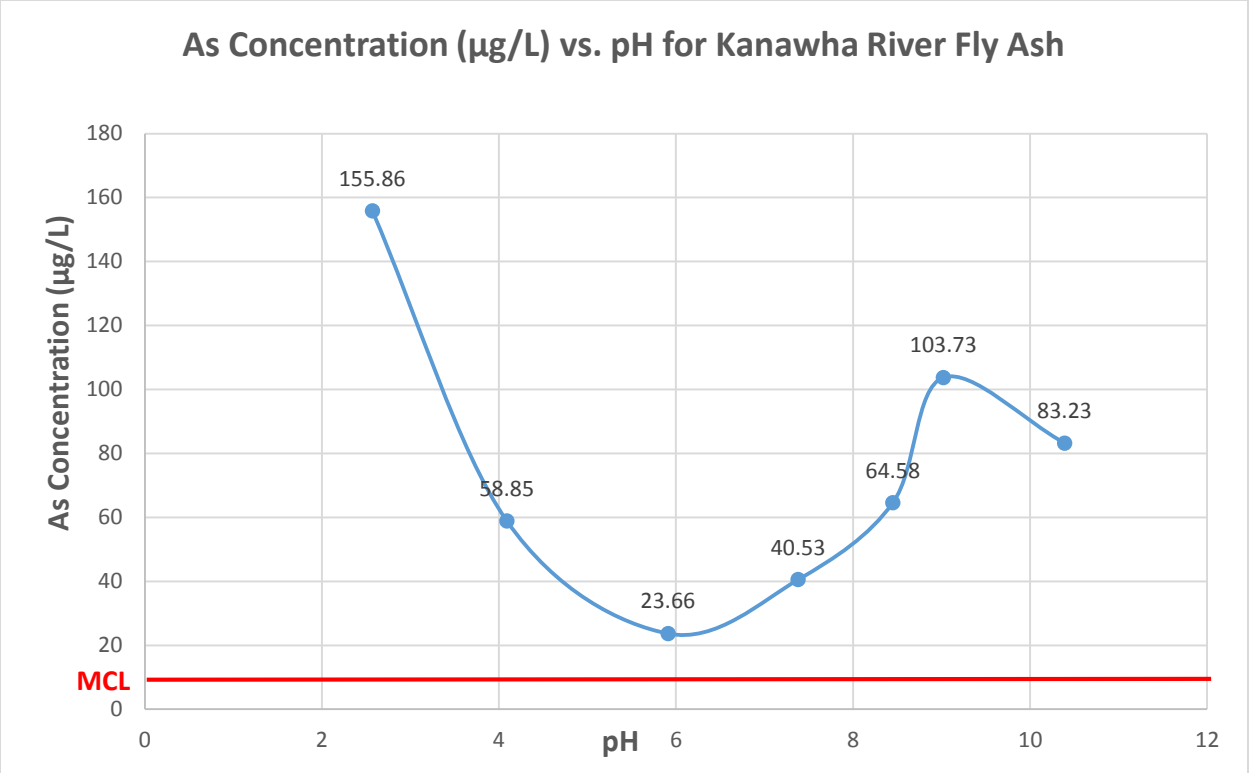

Figure 6. Liquid-Solid Partitioning Curve for Kanawha River Fly Ash

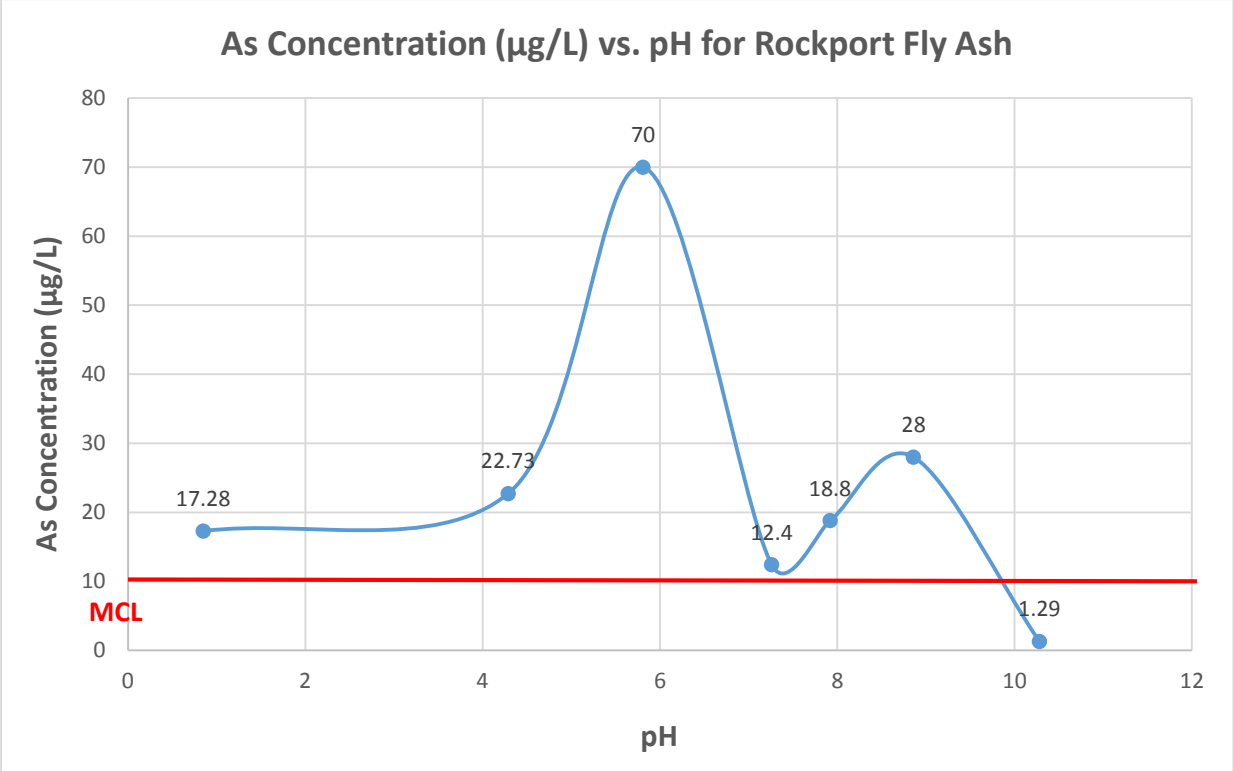

Figure 7. Liquid-Solid Partitioning Curve for Rockport Fly Ash

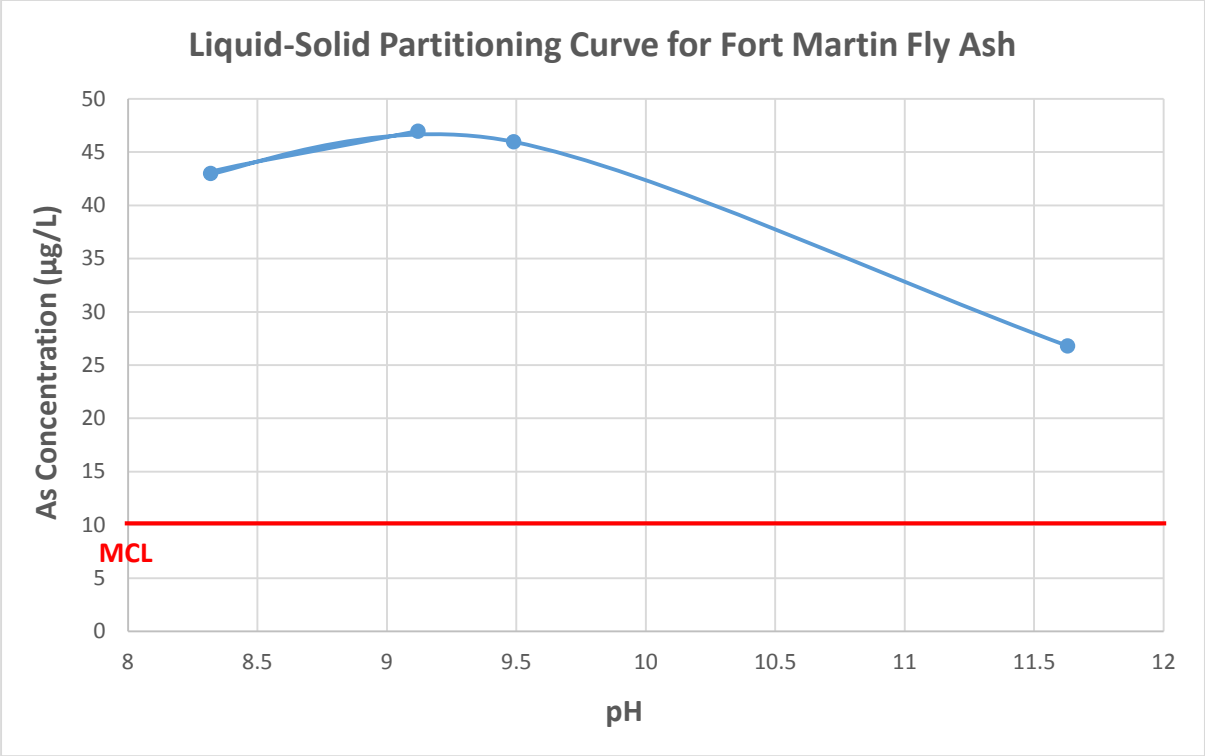

Figure 8. Liquid-Solid Partitioning Curve for Fort Martin Fly Ash

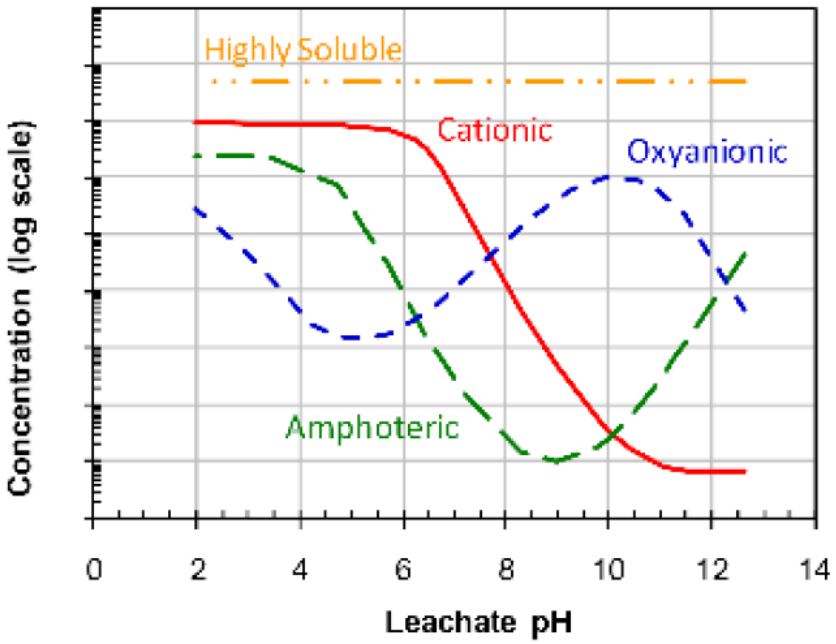

Figure 9. Characteristic LSP Curve Shapes

As an oxyanionic species, arsenic is characterized by a pH-dependent leaching and show maxima in the neutral to slightly alkaline range. The LSP curve for Kanawha River fly ash was a shift of characteristic LSP curve for oxyanionic species slightly to the lower pH. The LSP curve for Rockport fly ash was a shift of characteristic LSP curve for oxyanionic species slightly to the higher pH. The solubility of arsenic species must have been affected by factors other than the pH (i.e. other elements in the fly ash). One peak of solubility of Kanawha River fly ash was at around 9, with As (III) presented as $As(OH)_2^{2-}$and $As(O_3)^{3-}$ and As (V) as AsO_4^{3-}. The other maxima of solubility occured at pH of about 3, with $AsO_2(OH)_2^-$(As V) as dominant species. The plateau of maximum solubility for Rockport fly as was in the pH 5-7 range (neutral range), rich in $As(OH)_3$, $AsO_2(OH)_2^-$ and $AsO_3(OH)_2^{2-}$. Arsenic releases from acidic fly ash increase with pH, whereas in alkaline fly ash this trend is reversed (van der Hoek et al., 1994). This could be one explanation of the relatively low solubility in the high pH range for Rockport fly ash.

3.2 Column Test Analysis

Figure 10, 11 and 12 below provide plots of arsenic concentration in the liquid phase as a function of LS ratio for the three tested fly ash. For Rockport fly ash, the highest arsenic release occurred at the beginning of column test. The release concentration decreased and remained stable at low concentration level as LS ratio increases. For Fort Martin fly ash, the curve appears opposite to that for Rockport fly ash. For Kanawha River fly ash, column test could not continue after the first four intervals because of the backflow of leaching solution containing fly ash material. After the four intervals, inlet tube was blocked and the flow stopped. Two more attempts were made for column test of Kanawha River fly ash. However, the backflow and blocking of tube happened both times. It is suggested in the method that a solution of 1.0 mM calcium chloride in reagent water may be used when testing materials with either a high clay

content (to prevent deflocculation of clay layers) or high organic matter (to moderate mobilization of dissolved organic carbon). This suggestion was not aware of during the testing period. Therefore, a solution of 1.0 mM calcium chloride in reagent water should be tried for future column test of Kanawha River fly ash.

The variability of different patterns among the three fly ash samples can be due to adsorption processes and the interaction with other species, especially Ca. In the presence of notable amounts of Ca and alkaline pH, As release peak broadens and shifts towards higher L/S ratios. Such delayed response points to retention in secondary species controlling the solubility i.e. the precipitation of Ca-arsenate (Izquierdo & Querol, 2012). However, the curve for Rockport fly ash (with large amount of Ca and alkaline pH) did not agree with this trend while its initial pH was in the neutral range. Overall, concentrations of leached arsenic were very low (compared to those of the other two fly ash samples) for all cumulative LS ratios. This could have been affected by the original large amount of Ca (0.10g Ca/ g ash) in Rockport fly ash. The real peak might appear at higher LS ratio than the ones tested. Therefore, the influence of Ca on arsenic release is still noteworthy. The precipitation of ettringite at high pH would also account for the dramatic reduction in As in solution (Izquierdo & Querol, 2012). Result of X-ray diffraction for Rockport fly ash and shows that ettringite exited. Therefore, the overall low arsenic leaching from Rockport fly ash could have been affected by the existence of both large amount of Ca and ettringite. Results of X-ray diffraction for all three fly ash samples are provided in the Appendix.

The curve for Kanawha River fly ash (with relatively small amount of Ca and mildly alkaline pH), although not complete, also shows low overall release concentration. The amount of Ca in Kanawha River fly ash was notable, not as large as that in Rockport fly ash. Therefore, it is likely for the precipitation of Ca-arsenate to delay the arsenic release. For acidic fly ash, the Ca-

arsenate does not tend to precipitate (Izquierdo & Querol, 2012). Arsenic release concentrations were much higher from Fort Martin fly ash than those from Rockport and Fort Martin fly ash during the first 5 leaching intervals. This fact agrees with previous finding.

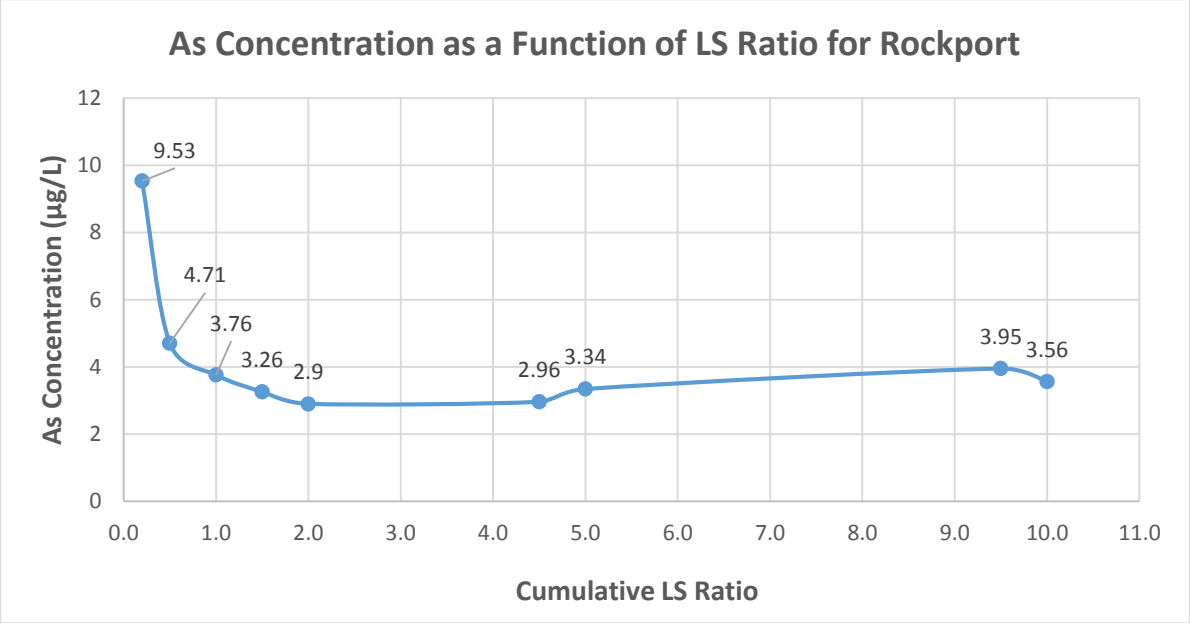

Figure 10. Arsenic Concentration as a Function of LS Ratio for Rockport Fly Ash

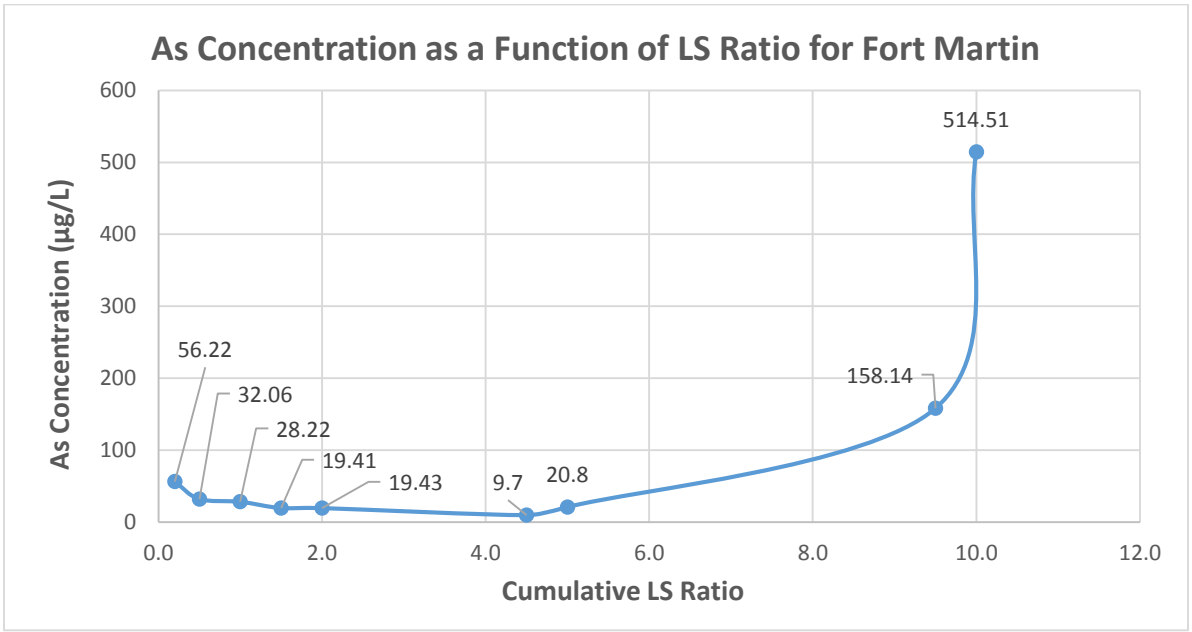

Figure 11. Arsenic Concentration as a Function of LS Ratio for Fort Martin Fly Ash

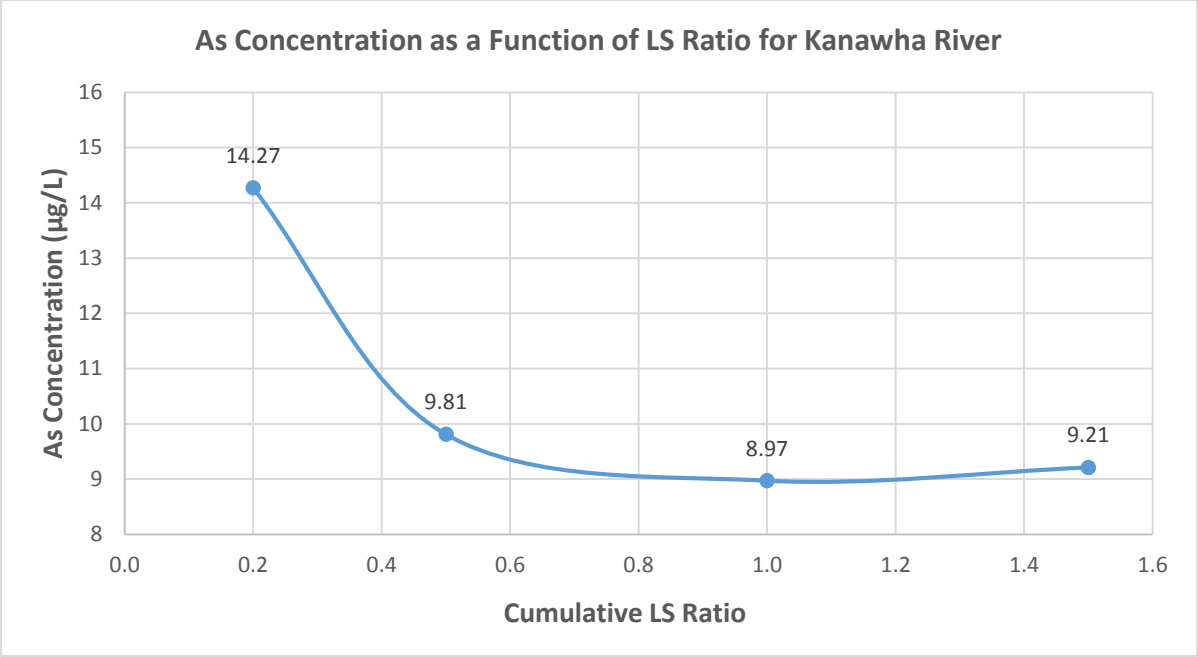

Figure 12. Arsenic Concentration as a Function of LS Ratio for Kanawha River Fly Ash

A noteworthy difference between arsenic concentrations of each fly ash was the considerably higher leaching concentration from Fort Martin fly ash. One possible reason for a higher concentration leached from Fort Martin fly ash is due to its initial ash pH. Research has shown that acidic fly ash were significantly richer in some inorganic constituents, including arsenic, than the alkaline fly ash (Donahoe & Neupane, 2012). Data shown in the above figures agrees with this. The minimum arsenic concentration leached from Fort Martin fly ash was higher than the peak arsenic concentration from Rockport fly ash which had an alkaline initial pH.

Figure 13, 14 and 15 provide the curves of cumulative mass release (in mg/kg-dry) as a function of cumulative LS ratio for all fly ash samples. The cumulative mass release of arsenic in to the liquid phase was calculated using equation:

$$\sum M_i = \sum_{i=1}^{9} \left[C_i \times \left(\sum L/S_i - \sum L/S_{i-1} \right) \right]$$

Where M_i = the cumulative mass release through interval i (mg/kg-dry)

C_i= the concentration of arsenic in the eluent collected during interval i (mg/L)

- $\sum L/S_i$ = the cumulative L/S of eluate collected through interval i (L/kg-dry)

- $\sum L/S_{i-1}$ = the cumulative L/S of eluate collected through interval i-1 (L/kg-dry)

Although not perfect, the curve for cumulative mass release as a function of cumulative LS ratio was overall linear for all three fly ash.

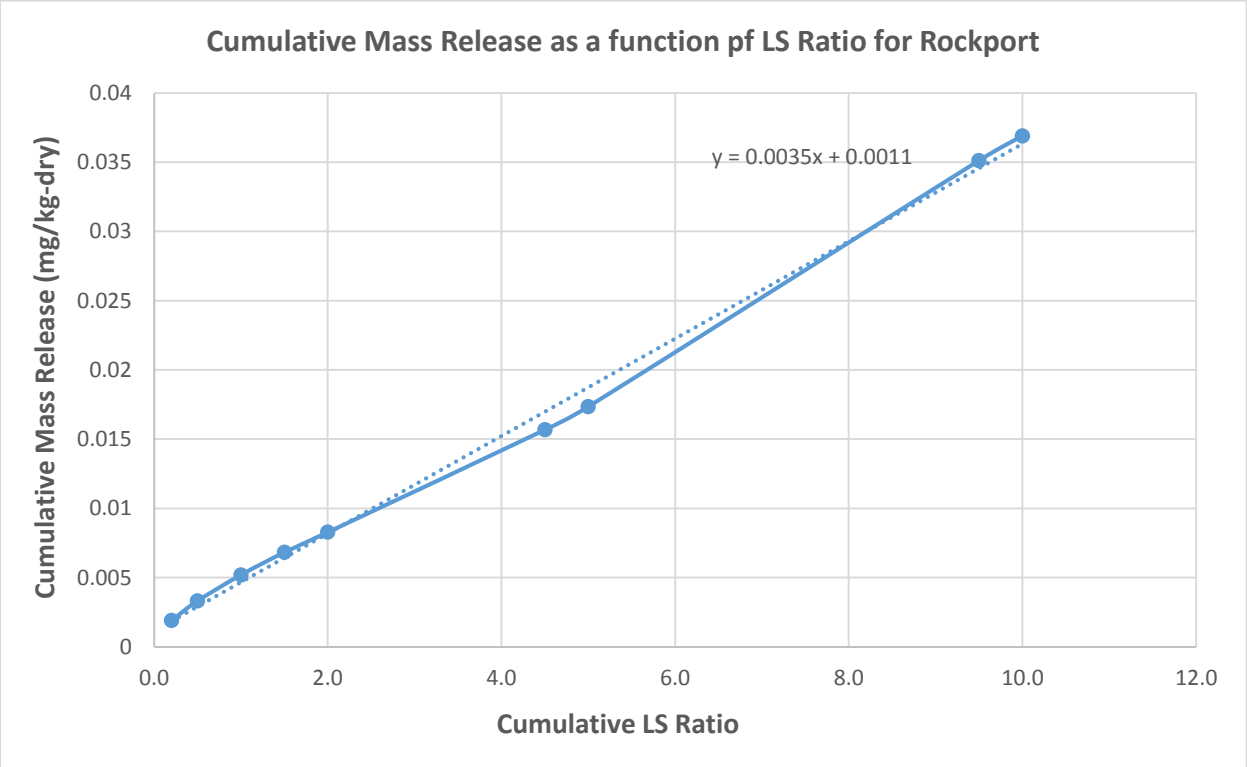

Figure 13. Cumulative Mass Release as a Function of Cumulative LS Ratio for Rockport Fly Ash

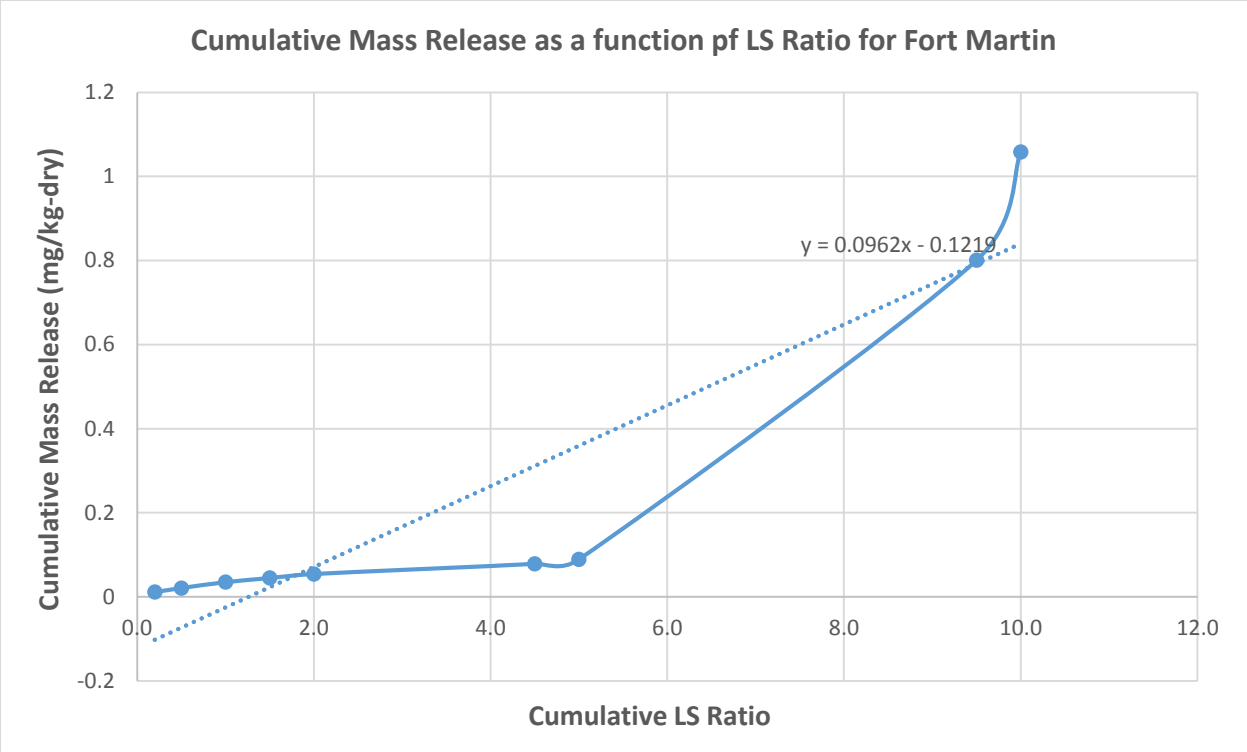

Figure 14. Cumulative Mass Release as a Function of Cumulative LS Ratio for Fort Martin Fly Ash

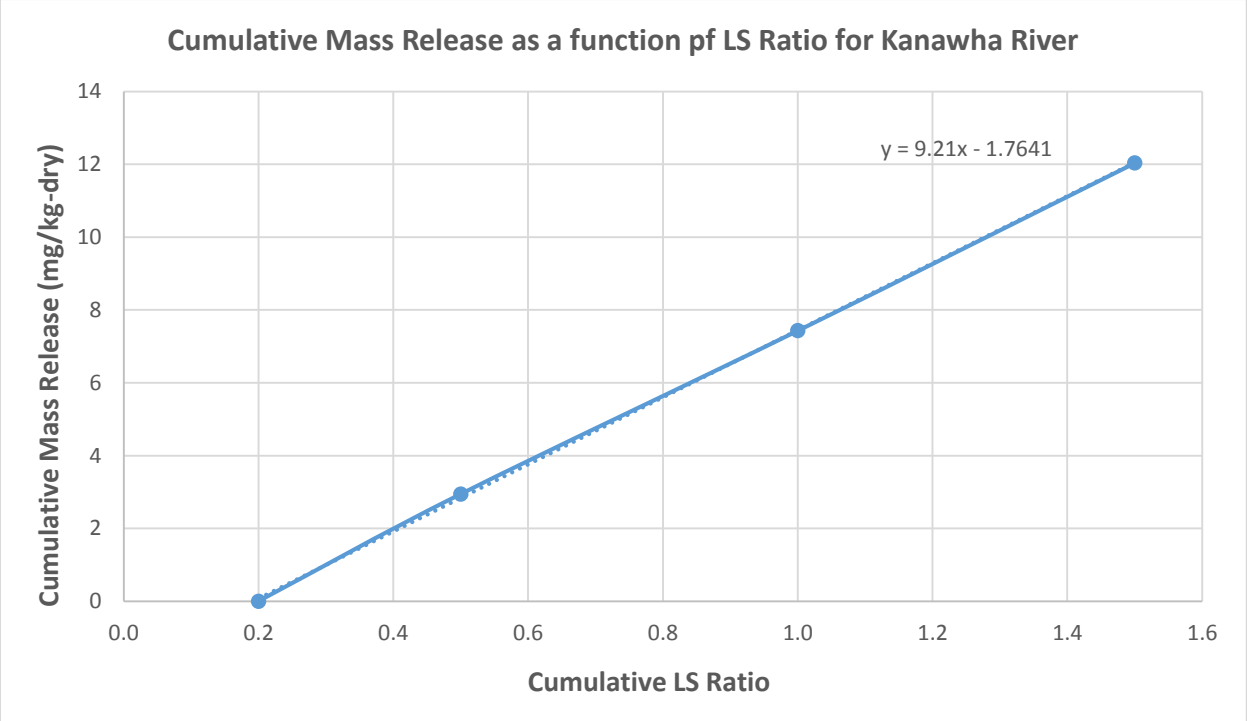

Figure 15. Cumulative Mass Release as a Function of Cumulative LS Ratio for Kanawha River Fly Ash

3.3 Mass Transfer Rate Analysis

Table 14 below provides the arsenic concentration for each leaching interval of the three fly ash. Knowing the concentration of each leaching interval, the interval mass release was calculated using equation:

$$M_{t_i} = \frac{C_i \times V_i}{A}$$

Where M_{t_i}= mass released during leaching interval i (mg/m^2)

C_i=arsenic concentration in the eluate for interval i (mg/L)

V_i=eluate volume in interval i (L)

A=external surface area of the compacted sample material exposed to the leaching solution (m^2)

The mean interval flux of arsenic in each interval as a function of the generalized mean of the square root of cumulative leaching time for each fly ash sample are provided below. The flux across the exposed surface of the sample was calculated using equation:

$$F_i = \frac{M_i}{t_i - t_{i-1}}$$

Where F_i= flux for interval i (mg/m^2·s)

M_i= mass released during the current leaching interval i (mg/m^2)

t_i= cumulative time at the end of the current leaching interval i (s)

t_{i-1}= cumulative time at the end of the previous leaching interval, i-1 (s)

The generalized mean of the square root of the cumulative leaching time was calculated using equation:

$$\overline{t_i} = \left(\frac{\sqrt{t_i} + \sqrt{t_{i-1}}}{2}\right)^2$$

Figure 16, 17 and 18 below show flux as a function of cumulative mean interval time of each fly ash are provided below. Tables including data for interval mass release, mean internal flux and mean interval time of each fly ash are provided in the appendix.

			Kanawha River fly ash	Rockport fly ash	Fort Martin fly ash
Interval Label	Interval Duration (d)	Cumulative Leaching Time (d)	As Concentration (µg/L)	As Concentration (µg/L)	As Concentration (µg/L)
T01	0.08	0.08	8.69	7.16	12.25
T02	0.92	1	8.65	6.57	13.64
T03	1	2	8.36	6.35	15.5
T04	5	7	8.67	5.64	16.95
T05	7	14	9.98	5.63	22.04
T06	14	28	10.82	5.95	30.23
T07	14	42	10.04	6.14	30.78
T08	7	49	9.74	5.87	34.59
T09	14	63	10.4	6.08	35.18

Table 14. Arsenic Concentration of Each Interval for All Fly Ash Samples

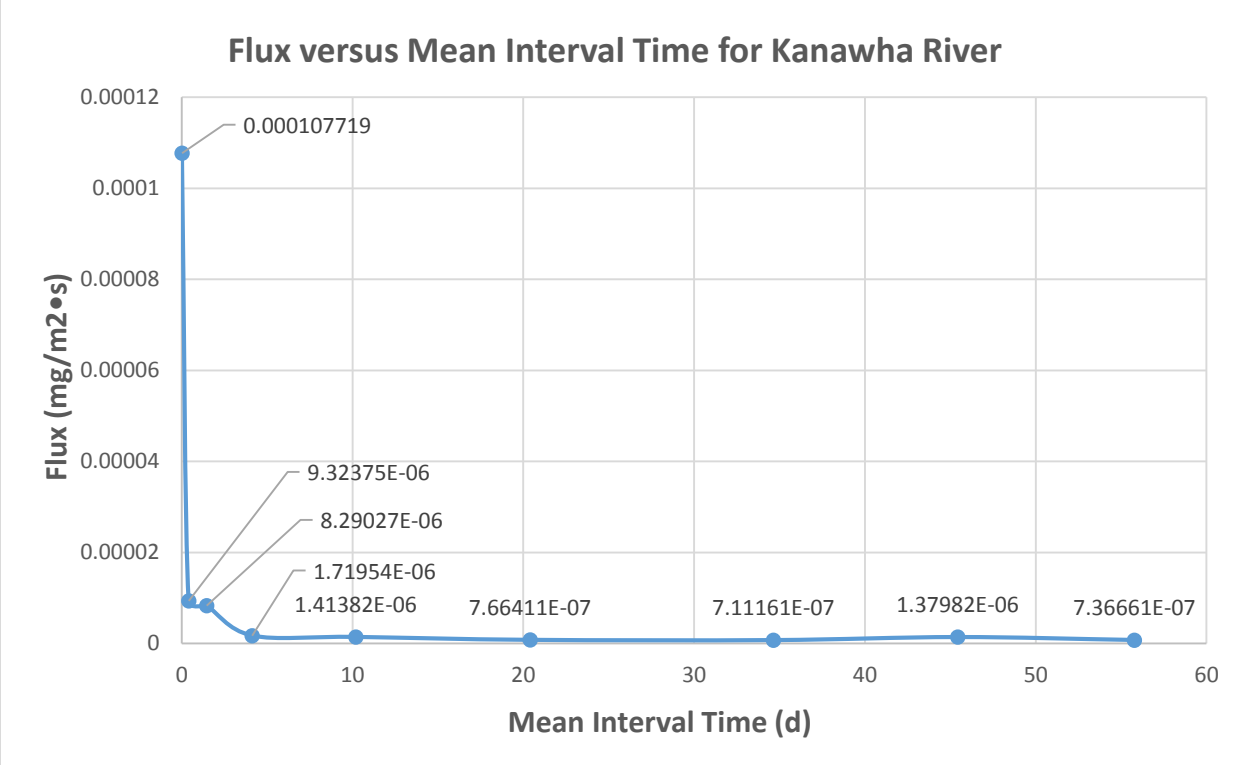

Figure 16. Flux versus Mean Interval Time for Kanawha River Fly Ash

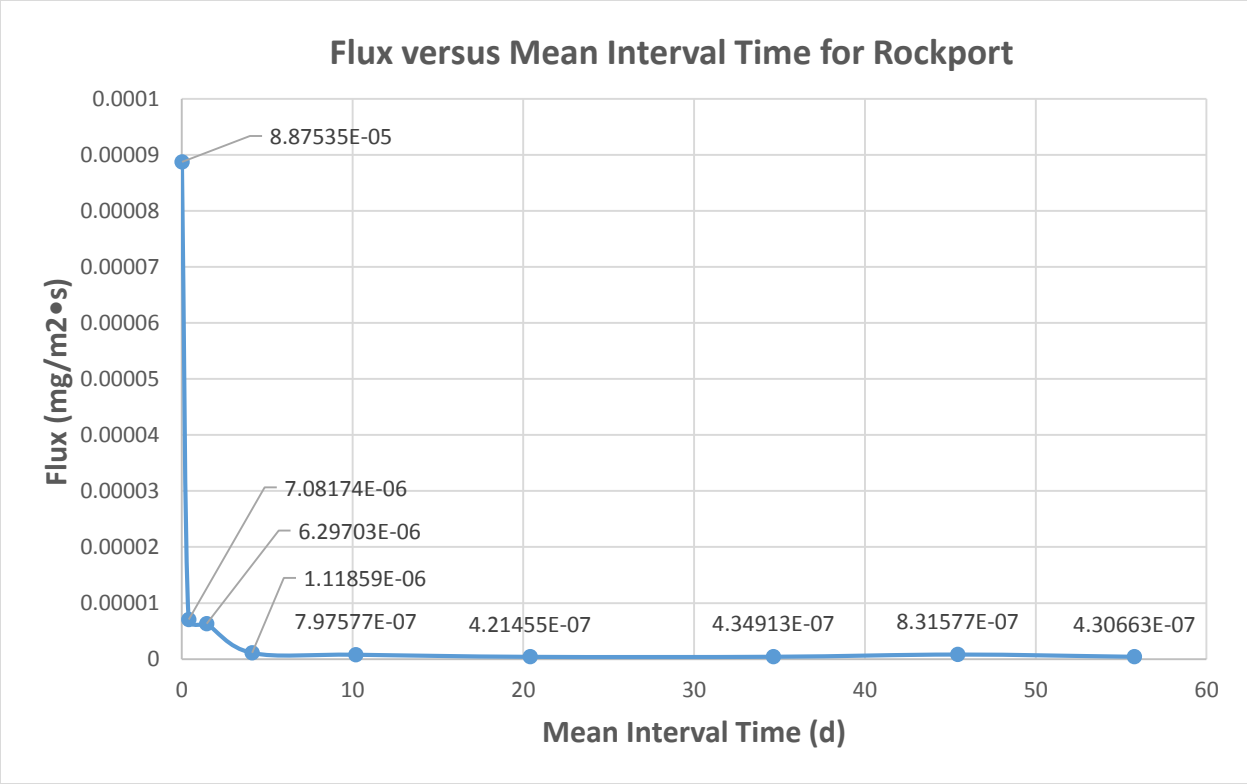

Figure 17. Flux versus Mean Interval Time for Rockport Fly Ash

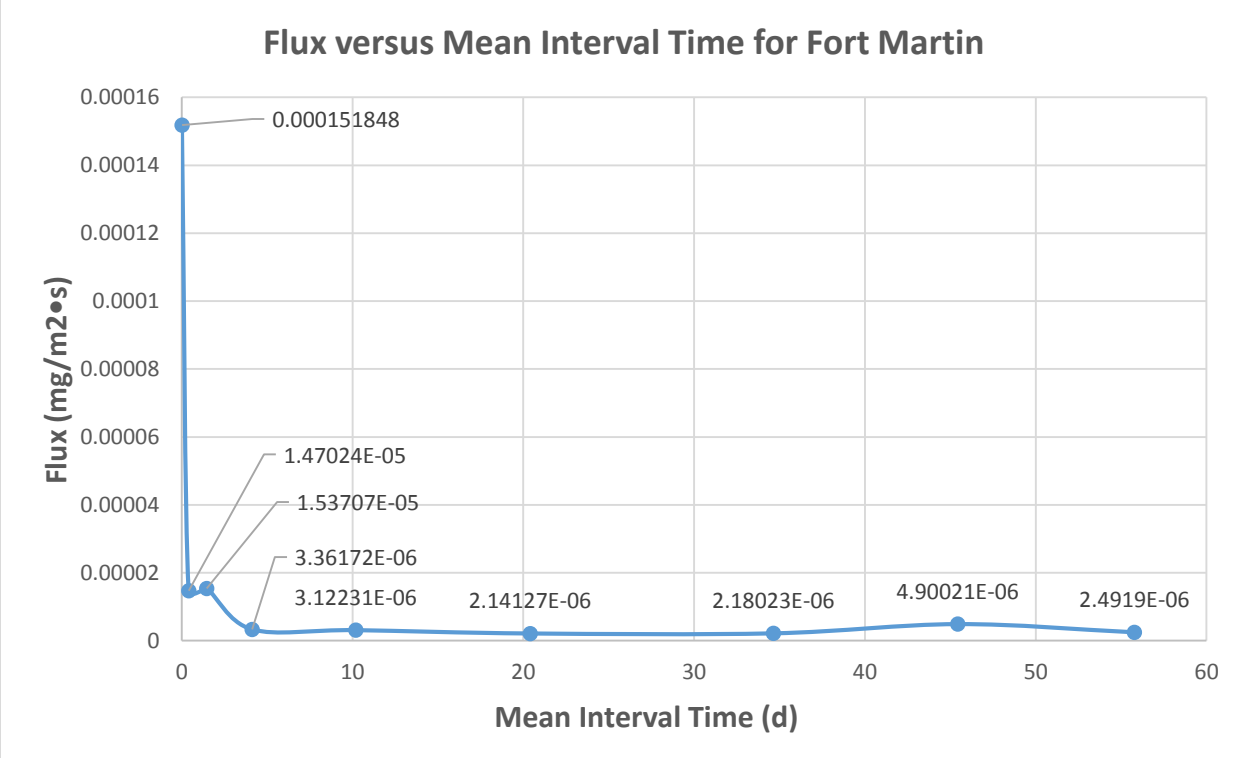

Figure 18. Flux versus Mean Interval Time for Fort Martin Fly Ash

For all three samples, the flux of arsenic from the liquid phase to the solid phase was at peak the first mean interval. The flux droped considerably after the first mean interval and remained stable at the lower level till the end of the diffusion test.

Mass release during each interval was summed to provide the cumulative mass release as a function of leaching time. Method 1315 provided interpretation of the cumulative release of constituents using the analytical solution for simple radial diffusion from a cylinder into an infinite bath (Hockley & van der Sloot, 1991). The mass release should be proportional to the square root of time for the simple radial diffusion model according to Method 1315. As shown in Figure 19, 20 and 21 below, the cumulative mass release was proportional to the square root of time for all three fly ash. Therefore, all three fly ash samples followed the simple radial diffusion model under diffusion-control conditions.

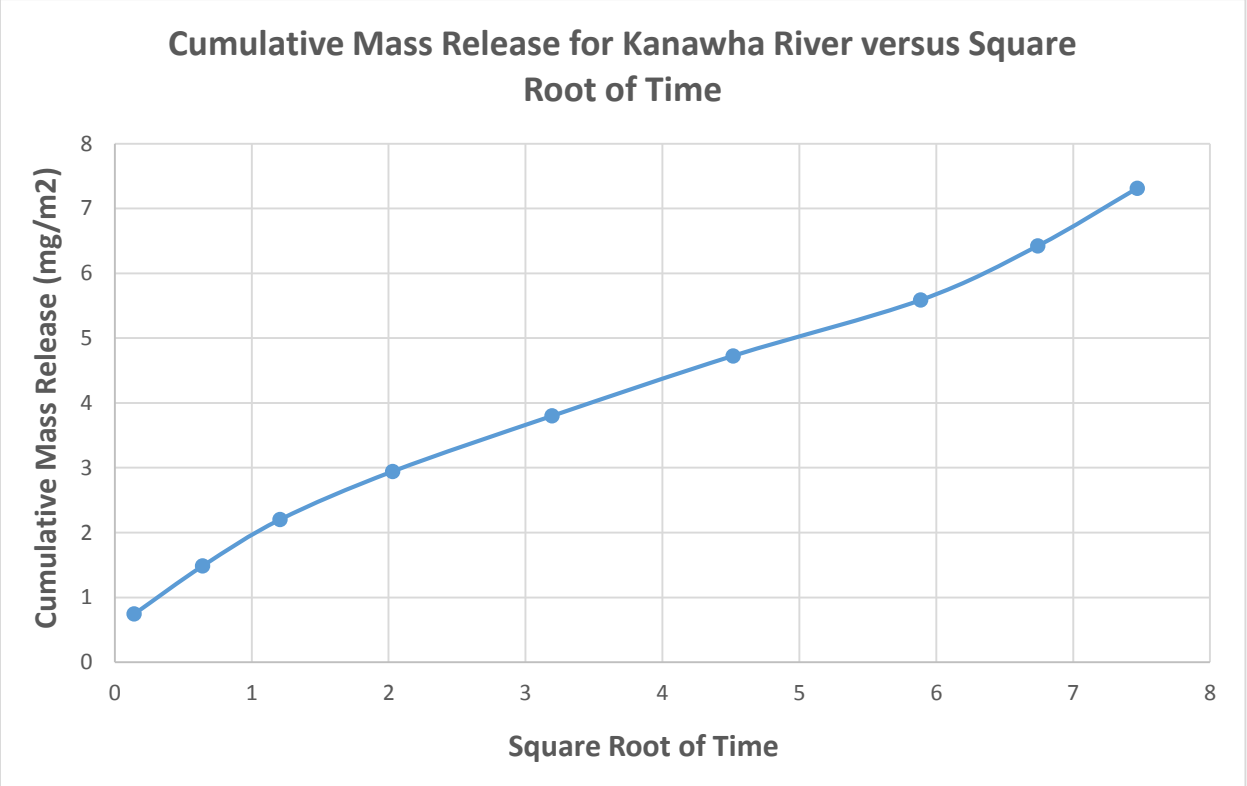

Figure 19. Cumulative Mass Release for Kanawha River Fly Ash versus Square Root of Time

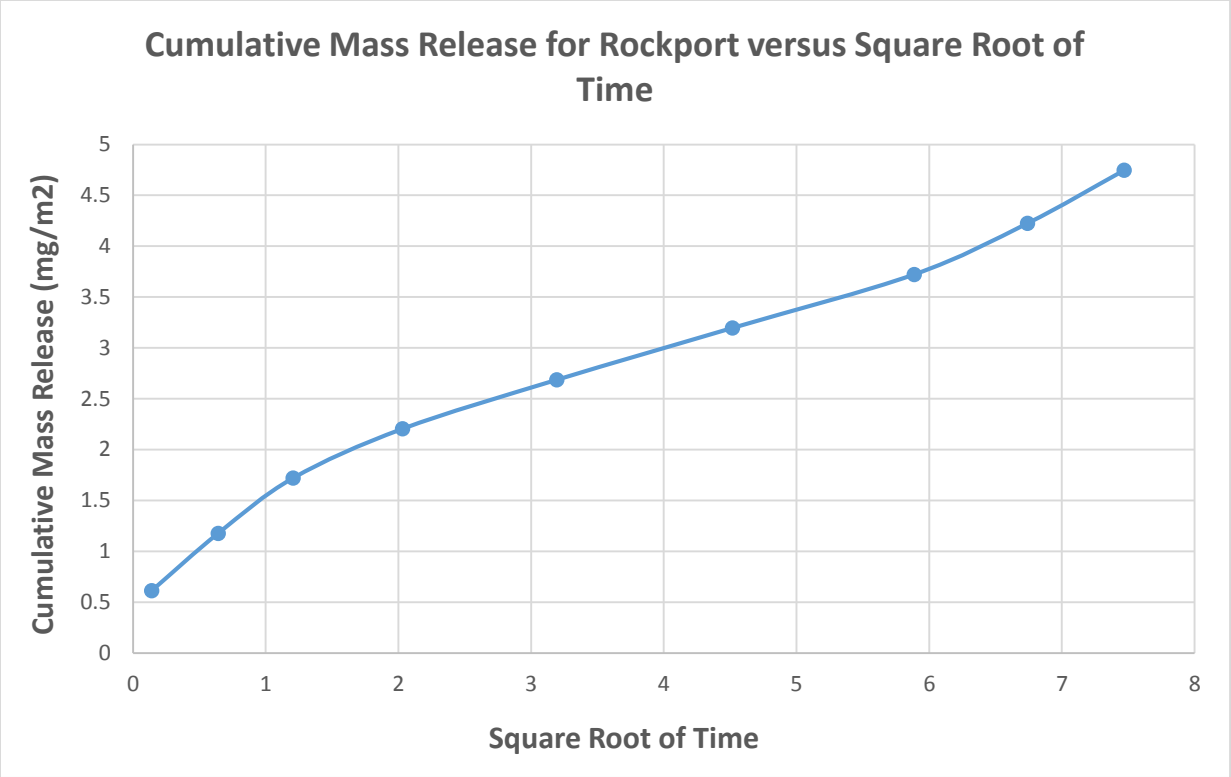

Figure 20. Cumulative Mass Release for Rockport Fly Ash versus Square Root of Time

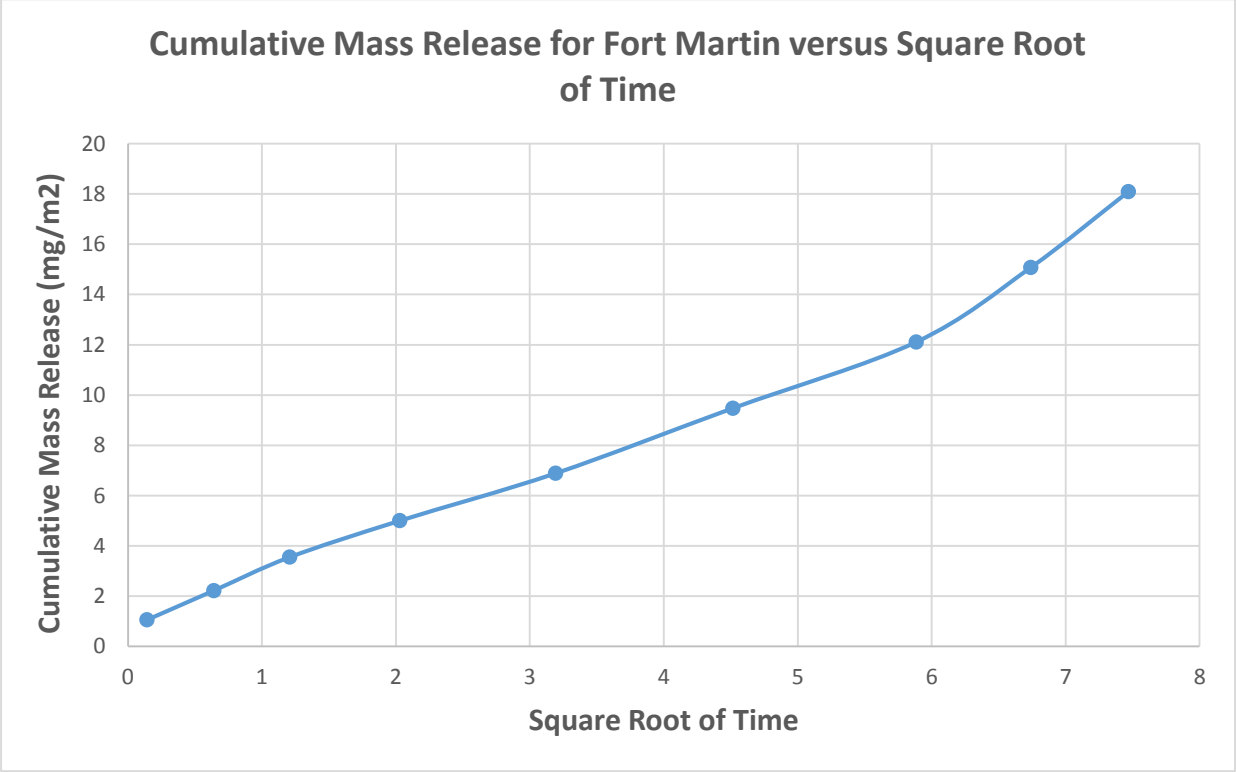

Figure 21. Cumulative Mass Release for Fort Martin Fly Ash versus Square Root of Time

Table 15 below provides the pH values of eluate for each interval. The average eluate pH for Kanawha River and Rockport were not very different from their initial pH. However, the average eluate pH of Fort Martin was far from its initial pH. According to the LSP curve of Kanawha River fly ash from Method 1313, arsenic leached into the liquid phase was at the lowest concentration when pH is around 6 (average eluate pH during tank leaching). Similar for Rockport fly ash, arsenic leached into the liquid phase was at the lowest concentration when pH was above 11 (average eluate pH during tank leaching). For Fort Martin fly ash, a complete LSP curve cannot be generated due to insufficient data. However, the leaching concentration was higher at the average eluate pH during tank leaching (8-9) than those of the other two fly ash samples at their average eluate pH. Therefore, The As concentrations shown in Table 14 above agree with result of LSP curves. As discussed in the above section, higher concentration leached from Fort Martin fly ash is probably due to its initial ash pH. Research has shown that acidic fly ash were significantly richer in some inorganic constituents, including arsenic, than the alkaline fly ash (Donahoe & Neupane, 2012). Data shown in Table 14 agrees with this. Arsenic leached from Fort Martin fly ash was much higher than that from Rockport fly ash which has an alkaline initial pH.

pH Value			
Cumulative Leaching Time (d)	Kanawha River	Rockport	Fort Martin
0.08	6.99	10.48	7.42
1	6.08	10.45	9.28
2	4.53	10.38	8.52
7	6.95	11.23	8.81
14	6.54	11.16	8.69
28	5.87	12.03	8.11
42	6.84	11.7	9.1
49	6.78	11.51	8.97
63	6.26	11.66	8.14

Table 15. pH value of Cumulative Leaching Time for All Fly Ash Samples

Chapter 4

Conclusion

The main goals for this research were achieved. The test for the solid-liquid partitioning of arsenic under a range of solution pH indicates that arsenic leaching from fly ash is highly pH-dependent. Arsenic condenses on the surface of fly ash after combustion in various forms with different solubility. At different pH range, leaching concentration depends on the solubility of different dominant As species. The study of the solid-liquid partitioning of arsenic as a function of solid-to-liquid ratio indicate the existence of other elements (i.e. Ca) in fly ash also influence arsenic leaching despite of initial ash pH. The test for the mass transfer rate of arsenic under diffusion-controlled release conditions show that the maximum flux usually occurs at the first leaching interval. Over time, arsenic leachate remains stable at a low level after the leaching of most arsenic from the contacting surface under diffusion-control condition. The simple radial diffusion model applies to all three fly ash.

The initial pH of the fly ash also influences the leaching behavior of arsenic. Results for method 1313 show arsenic release decreases as solution pH increases from fly ash with alkaline pH. This agree with previous research finding. In addition, results for Method 1314 and 1315 indicate higher arsenic leaching concentrations from acidic fly ash than those from alkaline fly ash, which also agrees with previous findings.

Future Work

To improve the test for LSP for Fort Martin fly ash, acid addition could be tried to obtain lower pH range although the ash is initially acidic. For column test of Kanawha River fly ash, a

solution of 1.0 mM calcium chloride in reagent water may be used instead of pure DI water in order to avoid backflow of solution with ash sample and the block of inlet tube. In addition, the result analysis may be improved with the element composition information of Fort Martin fly ash.

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Appendix

Kanawha River fly ash	
pH	As Concentration (µg/L)
10.39	83.23
9.02	103.73
8.45	64.58
7.38	40.53
5.91	23.66
4.09	58.85
2.57	155.86

Table A1. Arsenic Concentration and pH Values of Each Extraction for Kanawha River Fly Ash

Rockport fly ash	
pH	As Concentration (µg/L)
10.28	1.29
8.86	28
7.92	18.8
7.26	12.4
5.81	70
4.29	22.73
0.85	17.28

Table A2. Arsenic Concentration and pH Values of Each Extraction for Rockport Fly Ash

Fort Martin fly ash	
pH	As Concentration (µg/L)
11.63	26.8
9.49	45.97
8.32	43.01
9.12	46.98

Table A3. Arsenic Concentration and pH Values of Each Extraction for Fort Martin Ash

				11/1/14 10:30 AM	
Fraction Label	**Sum LS Ratio** [mL/g-dry]	**Fraction Volume** [mL]	**Day of Week**	**Scheduled Collection** Date/Time	**Actual Collection** Date/Time
-	0	10	*Sat*	11/1/14 10:54 AM	11/1/14 10:50 AM
T01	0.20	129	*Sat*	11/1/14 4:08 PM	11/1/14 4:30 PM
T02	0.50	209	*Sat*	11/2/14 1:04 AM	11/1/14 12:30 AM
T03	1.00	348	*Sun*	11/1/14 2:47 PM	11/2/14 3:00 PM
T04	1.50	348	*Sun*	11/3/14 5:17 AM	11/2/14 8:30 AM
T05	2.00	348	Mon	11/2/14 10:47 PM	11/3/14 10:30 PM
T06	4.50	1742	Thu	11/6/14 9:59 PM	11/6/14 10:10 PM
T07	5.00	348	Fri	11/7/14 12:28 PM	11/7/14 11:30 PM
T08	9.50	3136	Thu	11/13/14 8:10 AM	11/13/14 9:10 AM
T09	10.00	348	Thu	11/13/14 11:28 PM	11/13/14 11:33 PM

Table A4. Schedule d and Actual Collection Time and Date for Each Interval for Fort Martin Fly Ash

				10/6/14 7:09 PM	
Fraction Label	**Sum LS Ratio** [mL/g-dry]	**Fraction Volume** [mL]	**Day of Week**	**Scheduled Collection** Date/Time	**Actual Collection** Date/Time
-	0	10	Mon	10/6/14 7:30 PM	10/6/14 7:31 PM
T01	0.20	114	Mon	10/6/14 11:32 PM	10/6/14 11:14 PM
T02	0.50	186	Tue	10/7/14 5:48 AM	10/7/14 8:32 AM
T03	1.00	310	Tue	10/7/14 7:28 PM	10/7/14 7:55 PM
T04	1.50	310	Wed	10/8/14 6:51 AM	10/8/14 8:32 AM
T05	2.00	310	Wed	10/8/14 7:28 PM	10/8/14 7:31 PM
T06	4.50	1551	*Sat*	10/11/14 2:14 AM	10/11/14 12:10 AM
T07	5.00	310	*Sat*	10/11/14 11:06 AM	10/11/14 11:12 AM
T08	9.50	2791	Wed	10/15/14 1:42 PM	10/15/14 1:45 PM
T09	10.00	310	Thu	10/16/14 12:42 AM	10/16/14 1:05 PM

Table A5. Schedule d and Actual Collection Time and Date for Each Interval for Rockport Fly Ash

Kanawha River fly ash			
Fraction Label	Sum LS Ratio [mL/g-dry]	As Concentration (µg/L)	Cumulative Mass Release (mg/kg-dry)
T01	0.2	14.27	0.002854
T02	0.5	9.81	2.945854
T03	1.0	8.97	7.430854
T04	1.5	9.21	12.035854

Table A6. Arsenic Concentration and Cumulative Mass Release versus Cumulative LS Ratio for Kanawha River Fly Ash

Rockport fly ash			
Fraction Label	Sum LS Ratio [mL/g-dry]	As Concentration (µg/L)	Cumulative Mass Release (mg/kg-dry)
T01	0.2	9.53	0.001906
T02	0.5	4.71	0.003319
T03	1.0	3.76	0.005199
T04	1.5	3.26	0.006829
T05	2.0	2.9	0.008279
T06	4.5	2.96	0.015679
T07	5.0	3.34	0.017349
T08	9.5	3.95	0.035124
T09	10.0	3.56	0.036904

Table A7. Arsenic Concentration and Cumulative Mass Release versus Cumulative LS Ratio for Rockport Fly Ash

Fort Martin fly ash			
Fraction Label	Sum LS Ratio [mL/g-dry]	As Concentration (µg/L)	Cumulative Mass Release (mg/kg-dry)
T01	0.2	56.22	0.011244
T02	0.5	32.06	0.020862
T03	1.0	28.22	0.034972
T04	1.5	19.41	0.044677
T05	2.0	19.43	0.054392
T06	4.5	9.7	0.078642
T07	5.0	20.8	0.089042
T08	9.5	158.14	0.800672
T09	10.0	514.51	1.057927

Table A8. Arsenic Concentration and Cumulative Mass Release versus Cumulative LS Ratio for Fort Martin Fly Ash

Kanawha River fly ash							
Interval Label	Cumulative Leaching Time (s)	M_{t_i} (mg/m2)	F_i (mg/m2•s)	$\overline{t_i}$ (s)	$\overline{t_i}$ (d)	$\sqrt{t}$	Cumulative M_{t_i}
T01	6912	7.45E-01	0.000107719	1728	0.02	0.141421356	0.744553244
T02	86400	7.41E-01	9.32375E-06	35546.8	0.4114214	0.641421356	1.485679315
T03	172800	7.16E-01	8.29027E-06	125894	1.4571068	1.207106781	2.201958384
T04	604800	7.43E-01	1.71954E-06	356040	4.1208287	2.029982437	2.944798042
T05	1209600	8.55E-01	1.41382E-06	881258	10.199747	3.193704349	3.799877601
T06	2419200	9.27E-01	7.66411E-07	1762516	20.399495	4.516580004	4.726927785
T07	3628800	8.60E-01	7.11161E-07	2993451	34.646428	5.88612166	5.587148103
T08	4233600	8.35E-01	1.37982E-06	3925376	45.432592	6.740370349	6.421664627
T09	5443200	8.91E-01	7.36661E-07	4819426	55.780389	7.468626967	7.312729498

Table A9. Mass Release, Cumulative Mass Release, Flux and Mean Interval Time of Each Leaching Interval for Kanawha River Fly Ash

Rockport fly ash							
Interval Label	Cumulative Leaching Time (s)	M_{t_i} (mg/m2)	F_i (mg/m2•s)	$\overline{t_i}$ (s)	$\overline{t_i}$ (d)	$\sqrt{t}$	Cumulative M_{t_i}
T01	6912	6.13E-01	8.87535E-05	1728	0.02	0.141421356	0.613463892
T02	86400	5.63E-01	7.08174E-06	35546.8	0.4114214	0.641421356	1.176376989
T03	172800	5.44E-01	6.29703E-06	125894	1.4571068	1.207106781	1.720440636
T04	604800	4.83E-01	1.11859E-06	356040	4.1208287	2.029982437	2.203671971
T05	1209600	4.82E-01	7.97577E-07	881258	10.199747	3.193704349	2.686046512
T06	2419200	5.10E-01	4.21455E-07	1762516	20.399495	4.516580004	3.195838433
T07	3628800	5.26E-01	4.34913E-07	2993451	34.646428	5.88612166	3.721909425
T08	4233600	5.03E-01	8.31577E-07	3925376	45.432592	6.740370349	4.224847001
T09	5443200	5.21E-01	4.30663E-07	4819426	55.780389	7.468626967	4.745777234

Table A10. Mass Release, Cumulative Mass Release, Flux and Mean Interval Time of Each Leaching Interval for Rockport Fly Ash

Fort Martin fly ash							
Interval Label	Cumulative Leaching Time (s)	M_{t_i} (mg/m2)	F_i (mg/m2•s)	$\overline{t_i}$ (s)	$\overline{t_i}$ (d)	$\sqrt{t}$	Cumulative M_{t_i}
T01	6912	1.05E+00	0.000151848	1728	0.02	0.141421356	1.049571603
T02	86400	1.17E+00	1.47024E-05	35546.8	0.4114214	0.641421356	2.218237454
T03	172800	1.33E+00	1.53707E-05	125894	1.4571068	1.207106781	3.54626683
T04	604800	1.45E+00	3.36172E-06	356040	4.1208287	2.029982437	4.998531212
T05	1209600	1.89E+00	3.12231E-06	881258	10.199747	3.193704349	6.886903305
T06	2419200	2.59E+00	2.14127E-06	1762516	20.399495	4.516580004	9.476988984
T07	3628800	2.64E+00	2.18023E-06	2993451	34.646428	5.88612166	12.11419829
T08	4233600	2.96E+00	4.90021E-06	3925376	45.432592	6.740370349	15.07784578
T09	5443200	3.01E+00	2.4919E-06	4819426	55.780389	7.468626967	18.09204406

Table A11. Mass Release, Cumulative Mass Release, Flux and Mean Interval Time of Each Leaching Interval for Fort Martin Fly Ash

Sample ID	As	Ba	Be	Cd	Co	Cr	Li	Ni	Pb	Sb	Se	Si	Sr	Tl	V
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Rockport	32.657	4105.3	<0.000	1.855	36.591	69.8	4088.1	54.5	35.2	29.8	<0.012	2444.1	2122.2	<0.003	194.6
Kanawha River	36.324	489.0	<0.000	0.420	29.190	64.2	446.0	47.0	36.6	8.5	7.8	1679.7	243.9	<0.003	112.0

Sample ID	CVAF - Hg	P	K	Ca	Mg	S	Al	B	Cu	Fe	Mn	Mo	Na	Zn
	µg/kg	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Rockport	1000.0	3159.6	3766.4	104685.9	19443.3	7072.7	62462.4	550.6	145.0	28978.6	114.9	9.9	7117.7	118.9
Kanawha River	294.4	443.9	3374.2	3999.9	1364.4	1412.5	24605.6	30.4	67.5	11819.8	59.2	14.5	501.0	60.0

Table A12. Element Composition of Rockport and Kanawha River Fly Ash

Fly Ash	Minerals						
Fort Martin	Mullite (Al6Si2O13)	Magnesioferrite (MgFe2+3O4)	Gypsum (CaSO4!2H2O)	Quartz low (SiO2)	Ettringite (Ca6Al2(SO4)3 (OH)12!26H2O		
Kanawha River	Mullite (Al6Si2O13)	Gypsum (CaSO4!2H2O)	Quartz low (SiO2)	Hermatite (Fe2O3)			
Rockport	Mullite (Al6Si2O13)	Magnesioferrite (MgFe2+3O4)	Hermatite (Fe2O3)	Quartz low (SiO2)	Ettringite (Ca6Al2(SO4)3 (OH)12!26H2O	Calcite (CaCO3)	Gismondine (CaAl2Si2O8 !4H2O)

Table A13. Results for X-Ray Diffraction of All Fly Ash Samples